THERMAL DECOMPOSITION OF ORGANIC NITROGEN AND SULFUR COMPOUNDS

A Survey of Chemical Abstracts, 1930 to 1956

By Irven A. Jacobson, Jr.

* * * * * * * * * information circular 7947

March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Fred A. Seaton, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

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THERMAL DECOMPOSITION OF ORGANIC NITROGEN AND SULFUR COMPOUNDS [1]

A survey of Chemical Abstracts, 1930 to 1956

by

Irven A. Jacobson, Jr. [2]

INTRODUCTION

This literature survey consists of references dealing with gaseous state thermal decomposition reactions of organic nitrogen and sulfur compounds. The reference source for the survey was the Chemical Abstracts from 1930 to 1956, inclusive. Original articles were not studied. The starting date was set at 1930 because previous to this time much of the work is questionable.

This report is in three parts: Part I lists nitrogen compounds; Part II, sulfur compounds; and Part III, compounds containing both nitrogen and sulfur. The organization of the classes of compounds is alphabetical: Part I - amides, amines, amino acids, ammonia, azides, azines, azo compounds, heterocyclic nitrogen compounds, hydrazine, nitrates, nitriles, nitrites, nitro compounds and miscellaneous nitrogen compounds; Part II - disulfides, sulfides (including double and triple sulfides), thiols, thiophenes and xanthates; Part III - thioacid amides, thiazoles, thiocyanates and thiuram disulfides. A class formula is included with each class name. The R's used in these class formulas may refer to hydrogen or to the same or different radicals when more than one R appears.

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[1] Manuscript completed August 1959

[2] Chemist, Bureau of Mines, Region III, Laramie, Wyoming

Original from THE OHIO STATE UNIVERSITY

The scheme used for presenting the data is as follows:

I. Class name

A. Type of compound (aliphatic or aromatic)

1. Specific compound name

a. Reference

Data concerning the reaction.

To preserve this scheme, the report deviates from the correct outline form by using single headings and subheadings. Specific compounds in each type have been listed in order of increasing molecular weight. The references in the text consist of the author's name, year of publication and a bibliography reference in parenthesis. If the reference is a patent, the letter P is used after the date.

The information available in the abstracts is in the following order: Reaction, temperature in degrees centigrade, pressure in millimeters of mercury, type of reaction (first-order, uni- or bimolecular, homo- or heterogeneous, free-radical or chain-type reaction), the activation energy or the Arrhenius equation, catalyst and miscellaneous information.

ACKNOWLEDGMENTS

This report was prepared as part of the oil-shale program of the Bureau of Mines at the Laramie Petroleum Research Center, Laramie, Wyoming. Thanks are extended to H. B. Jensen for assistance in the final organization of the information. This work was done under a cooperative agreement between the University of Wyoming and the Bureau of Mines, U. S. Department of the Interior.

PART I

NITROGEN COMPOUNDS

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Part I

NITROGEN COMPOUNDS

I. AMIDES

[RCONR$_2$]

A. Aliphatic amides

1. Formamide

a. SCHWAB, G. M., 1950 (108)

$HCONH_2 \rightarrow NH_3 + CO_2$

The reaction was unimolecular,

$k = 10^{(14.2 \pm .5)}$ exp. $-(39,400 \pm 1,000)/RT$ sec.$^{-1}$

C, Pt, Ag, Ni, Cu and Al_2O_3 had no effect as catalysts but Zn changed the reaction.

Reactions with Zn as catalyst:

$HCONH_2 \rightarrow NH_3 + CO_2$

$HCONH_2 \rightarrow HCN + H_2O$

$HCONH_2 \rightarrow HOCN^{\cdot} + H_2$

$HOCN^{\cdot} + NH_3 \rightarrow CO(NH_2)_2$

$2CO(NH_2)_2 \rightarrow NH(CONH_2)_2 + NH_3$

$2HCONH_2 + Zn \rightarrow Zn(HNCHO)_2 + H_2$

2. Acetamide

a. DAVIDSON, D., and KARTEN, M., 1956 (31)

$CH_3CONH_2 \rightarrow NH_3 + CH_3COOH + CH_3CN + H_2O$

Temperature of 217 to 220°

Heated for 3.5 hours.

3. Propionamide

a. DAVIDSON, D., and KARTEN, M., 1956 (31)

$C_2H_5CONH_2 \longrightarrow NH_3 + C_2H_5COOH + C_2H_5CN +$
$C_2H_5CONHCOC_2H_5$

Temperature of 217 to 225°

Heated for 3.5 hours.

4. Isobutyramide

a. DAVIDSON, D., and KARTEN, M., 1956 (31)

$(CH_3)_2CHCONH_2 \longrightarrow NH_3 + (CH_3)_2CHCOOH + (CH_3)_2CHCN +$
$(CH_3)_2CHCONHCOCH(CH_3)_2$

Temperature of 213 to 220°

Heated for 3 hours.

5. Butyramide

a. DAVIDSON, D., and KARTEN, M., 1956 (31)

$CH_3CH_2CH_2CONH_2 \longrightarrow NH_3 + CH_3CH_2CH_2COOH +$
$CH_3CH_2CH_2CN$

Temperature of 217 to 227°

Heated for 3.5 hours.

6. Hexanamide

a. DAVIDSON, D., and KARTENS, M., 1956 (31)

$CH_3(CH_2)_4CONH_2 \longrightarrow NH_3 + CH_3(CH_2)_4COOH +$
$CH_3(CH_2)_4CN$

Temperature of 207 to 252°

Heated for 2.5 and 5 hours.

7. N, N-Dimethyl lactamide acetate

   a. RATCHFORD, W. P., and FISHER, C. H., 1947 (94)

      $CH_3CH(OOCCH_3)CON(CH_3)_2 \longrightarrow CH_2{:}CHCON(CH_3)_2 + CH_3COOH +$

      small amounts of H_2O, H_2, CO, and $(CH_3CO)_2$

      Temperature of 500 to 560°

8. N-Alkyl-β-alkoxypropionamide

   a. ERICKSON, J. G., 1950P (37)

      $ROCH_2CH_2CONHR' \longrightarrow CH_2{:}CHCONHR'$

      Used alumina, silica gel, etc., as catalysts.

9. Dibutyladipamide

   a. GOODMAN, I., 1955 (39)

      Nylon 66 ⟶ decomposition products

      No products listed. Abstract stated that many had been identified.

B. Aromatic amides

1. Benzamide

   a. DAVIDSON, D., and KARTEN, M., 1956 (31)

      $C_6H_5CONH_2 \longrightarrow NH_3 + C_6H_5COOH + C_6H_5CN$

      Temperature of 228 to 284°

      Heated for 3.5 hours.

2. 2-Phenylacetamide

   a. DAVIDSON, D., and KARTEN, M., 1956 (31)

      $C_6H_5CH_2CONH_2 \longrightarrow NH_3 + C_6H_5CH_2COOH + C_6H_5CH_2CN$

      Temperature of 244 to 279°

      Heated for 4.5 hours.

II. AMINES

[R_3N]

A. Aliphatic amines

1. Methylamine

a. JOLLEY, L. J., 1934 (53)

$CH_3NH_2 \longrightarrow HCN + 2H_2$

$CH_3NH_2 + H_2 \longrightarrow CH_4 + NH_3$

Temperature of 500°

b. EMELEUS, H. J., and JOLLEY, L. J., 1935 (36)

$CH_3NH_2 \longrightarrow HCN + 2H_2$

$CH_3NH_2 + H_2 \longrightarrow CH_4 + NH_3$

The first reaction was unimolecular and homogeneous with a large activation energy. The second reaction was heterogeneous.

Both reactions started with the free-radical reaction:

$CH_3NH_2 \longrightarrow CH_3^{\cdot} + NH_2^{\cdot}$

c. CARTER, A. G., BOSANQUET, P. A., SILOCKS, C. G., TRAVERS, M. W., and WILSHIRE, A. F., 1939 (20)

Temperature of 500°

The reaction was heterogeneous.

d. TRAVERS, M. W., and HAWKED, J. A., 1939 (141)

Temperature of 530°

Added nitric oxide in increasing amounts. Hydrogen formation was inhibited until the hydrogen formation equaled the methane formation. Methane formation was not inhibited.

2. Dimethylamine

a. TAYLOR, H. A., 1932 (129)

Temperature of 480 to 510°

Pressure of 3.75 to 600 mm.

The reaction was unimolecular and homogeneous with an activation energy of 44,300 cal./mole.

The reaction was measured by pressure increase and found to be complex.

b. CARTER, A. G., BOSANQUET, P. A., SILOCKS, C. G., TRAVERS, M. W., and WILSHIRE, A. F., 1939 (20)

$2(CH_3)_2NH \longrightarrow CH_4 + CH_3N{:}CH_2 + CH_3NH_2 +$ small amounts of H_2

The reaction was first-order and a chain reaction.

Packing decreased CH_4 formation.

c. TRAVERS, M. W., and HAWKED, J. A., 1939 (141)

Temperature of 420°

Added nitric oxide.

Large amounts needed for inhibition. CH_4 and H_2 formation were inhibited by the same amount.

3. Trimethylamine

a. CARTER, A. G., BOSANQUET, P. A., SILOCKS, C. G., TRAVERS, M. W., and WILSHIRE, A. F., 1939 (20)

$(CH_3)_3N \longrightarrow CH_4 + CH_3N{:}CH_2 +$ small amounts of H_2 and C_2H_6

Temperature of 400°

First-order, chain reaction with an activation energy of 59,000 cal./mole.

Methyl radicals were the chain carriers.

Packing decreased the reaction rate.

Helium increased the CH_4 production.

b. TRAVERS, N. W., and HAWKED, J. A., 1939 (141)

Temperature of 420°

Added nitric oxide.

Hydrogen formation was initially inhibited more than the CH_4 formation.

4. Ethylamine

a. TAYLOR, H. A., 1930 (127)

Temperature of 500 to 540°

Pressure of 50 to 400 mm.

The reaction was unimolecular and homogeneous with an activation energy of 43,400 cal./mole.

b. SCHUMACHER, H. J., and WIIG, E. O., 1932 (107)

$C_2H_5NH_2 \longrightarrow N_2 + H_2 + CH_4 + NH_3 + \text{oils}$

Temperature of 510 to 535°

Pressure of 100 to 600 mm.

The reaction was a unimolecular, heterogeneous chain reaction.

The reaction was affected by water and nitrogen.

c. TAYLOR, H. A., and DITMAN, J. G., 1936 (132)

$2C_2H_5NH_2 \longrightarrow C_2H_5NH.NHC_2H_5 + H_2$

$C_2H_5NH.NHC_2H_5 \longrightarrow N_2 + H_2 + 2C_2H_5^{\cdot}$

$C_2H_5^{\cdot} \longrightarrow CH_4 + C_4H_{10}$ + unsaturated hydrocarbons

The first reaction was bimolecular with no volume change, the second reaction was a first-order chain reaction.

5. Diethylamine

a. TAYLOR, H. A., and HERMAN, C. R., 1935 (133)

$(C_2H_5)_2NH \longrightarrow C_2H_5NH.NHC_2H_5 + C_4H_{10}$

$C_2H_5NH.NHC_2H_5 \longrightarrow N_2 + H_2 + 2C_2H_5^{\cdot}$

$C_2H_5^{\cdot} \longrightarrow CH_4 + C_4H_{10}$ + unsaturated hydrocarbons

Temperature of 510 to 540°

Pressure of 15 to 400 mm.

The reaction was measured by pressure increase.

6. Triethylamine

a. TAYLOR, H. A., and JUTERBOCK, E. E., 1935 (135)

$(C_2H_5)_3N \longrightarrow (C_2H_5)_2N.N(C_2H_5)_2 + C_4H_{10}$

$(C_2H_5)_2N.N(C_2H_5)_2 \longrightarrow$ decomposition products

Temperature of 450 to 500°

Pressure of 15 to 400 mm.

The reaction was homogeneous with an activation energy of 50,000 cal./mole.

7. Propylamine

   a. TAYLOR, H. A., and ACHILLES, H. R., 1931 (130)

      Temperature of 520 to 580°

      Pressure of 36 to 597 mm.

      The reaction was unimolecular and homogeneous with an activation energy of 44,600 cal./mole.

   b. SICKMAN, D. V., and RICE, O. K., 1935 (111)

      Pressure below 4 mm.

      The reaction was first order.

      The reaction was inhibited by Pyrex and was thought to be a chain reaction.

8. Isopropylamine

   a. TAYLOR, H. A., 1932 (128)

      Temperature of 480 to 510°

      Pressure of 3.75 to 600 mm.

      The reaction was unimolecular and homogeneous.

      The reaction was complex and was measured by pressure increase.

9. Butylamine

   a. BEACHELL, H. C., and TAYLOR, H. A., 1942 (10)

$$C_4H_9NH_2 \longrightarrow C_4H_9NH^{\cdot} + H^{\cdot}$$

$$C_4H_9NH_2 + H^{\cdot} \longrightarrow C_4H_9NH^{\cdot} + H_2$$

$$2C_4H_9NH^{\cdot} \longrightarrow C_4H_8{:}NC_4H_9 + NH_3$$

$2C_4H_9NH^{\cdot} \longrightarrow C_4H_9NH_2 + C_4H_9N:$

$C_4H_9N: \longrightarrow C_3H_8 + HCN$

The reaction had an activation energy of 89,000 cal./mole.

The reaction was measured by pressure increase.

10. tert-Butylamine

a. PRITCHARD, H. O., SOWDEN, R. G., and TROTMAN-DICKENSON, A. F., 1954 (92)

$(CH_3)_3CNH_2 \longrightarrow (CH_3)_2C{:}CH_2 + NH_3$

$(CH_3)_3CNH_2 \longrightarrow CH_4 + C_3H_7N$

Temperature of 493 to 541°

Pressure of 50 to 180 mm.

The reaction was first-order and homogeneous,

$k = 10^{14.79} \text{ exp. } -(67,100/RT) \text{ sec.}^{-1}$

The reaction was studied by the static method.

The initial reaction was fast. The over-all reaction gave a NH_3 to CH_4 ratio of 1 to 2.5. Exact nature of C_3H_7N was not determined.

11. 1,3-Dimethylbutylamine

a. BALANDIN, A. A., and VASYUNINA, N. A., 1955 (6)

$(CH_3)_2CHCH_2CH(NH_2)CH_3 \longrightarrow$ dehydrogenation

Temperature of 270 to 330°

With Pd-asbestos catalyst the rate constant varied from 5.13 to 12.7 min.$^{-1}$ and the activation energy was 9,920 cal./mole.

With Ni on Al_2O_3 as catalyst the rate constants varied from 7 to 17.37 min.$^{-1}$ and the activation energy was 9,550 cal./mole.

12. 1-Methyl-2, 2-dimethylpropylamine

a. BALANDIN, A. A., and VASYUNINA, N. A., 1955 (6)

$(CH_3)_2CCH(CH_3)NH_2 \longrightarrow$ dehydrogenation and deamination

Temperature of 400 to 450°

Activation energy for dehydrogenation was 18, 130 cal. /mole, for deamination, 17, 340 cal. /mole.

Catalyst was ThO_2.

13. 1-Methylhexylamine

a. BALANDIN, A. A., and VASYUNINA, N. A., 1955 (6)

$CH_3(CH_2)_4CH(CH_3)NH_2 \longrightarrow$ dehydrogenation

Temperature of 270 to 330°

With Pd-asbestos catalyst, the rate constant varied from 3. 83 to 8. 56 min. $^{-1}$ with an activation energy of 9, 720 cal. /mole.

With Ni on Al_2O_3 as catalyst the rate constant varied from 6. 92 to 17. 7 min. $^{-1}$ with an activation energy of 9, 370 cal. /mole.

14. 2, 4-Dimethyl-3-aminopentane

a. BALANDIN, A. A., and VASYUNINA, N. A., 1955 (6)

$(CH_3)_2CHCH(NH_2)CH(CH_3)_2 \longrightarrow$ dehydrogenation

Temperature of 270 to 330°

With Pd-asbestos catalyst, the rate constant varied from 5.26 to 15. 7 min. $^{-1}$ with an activation energy of 9, 140 cal. /mole.

With Ni on Al_2O_3 as the catalyst the rate constant varied from 5. 38 to 11. 94 min. $^{-1}$ with an activation energy of 8, 680 cal. /mole.

B. Aromatic amines

1. Benzylamine

a. HOWARD, L. B., HILBERT, G. E., and GADDY, V. L. 1932 (49)

$C_6H_5CH_2NH_2 \longrightarrow$ tetraphenylpyrrole + 2, 4, 5-triphenylimidazole

b. SZWARC, M., 1949 (124)

$C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2^{\cdot} + NH_2^{\cdot}$

$C_6H_5CH_2^{\cdot} + NH_2^{\cdot} \xrightarrow{\text{toluene}} (C_6H_5CH_2)_2 + NH_3$

The reaction was first-order and unimolecular,

$k = 6 \times 10^{12}$ exp. -(59, 400/RT) sec. $^{-1}$

The reaction was studied by the flow method using toluene as a carrier gas.

c. SZWARC, M., 1949 (126)

$C_6H_5CH_2NH_2 \longrightarrow NH_3 + (C_6H_5CH_2)_2$ + small amounts of H_2

Temperature of 650 to 800°

The reaction was first-order and homogeneous with an activation energy of 59, 000 ± 4, 000 cal. /mole.

The reaction was studied by the flow method using toluene as a carrier gas.

The ammonia to bibenzyl ratio was 1 to 1.

The heat of formation of NH_2 radical was 35, 500 cal. /mole.

2. Dibenzylamine

a. HOWARD, L. B., HILBERT, G. E., and GADDY, V. L., 1932 (49)

$(C_6H_5CH_2)_2NH \longrightarrow$ tetraphenylpyrrole + 2, 4, 5-triphenylimidazole

3. 1-Phenylpropylamine

   a. BALANDIN, A. A., and VASYUNINA, N. A., 1955 (6)

      $C_6H_5CH(NH_2)CH_2CH_3$ ⟶ dehydrogenation and deamination

      Temperature of 360 to 430°

      Activation energy for the dehydrogenation reaction was 5,160 cal./mole. for the deamination it was 5,360 cal./mole.

      Used ThO_2 for catalyst.

4. 2'-Amino-2-azidoacetophenone

   a. BOYER, J. H., and STRAW, D., 1953 (16)

      $o\text{-}H_2NC_6H_4COCH_2N_3 \longrightarrow$ indigo

5. 1-Anilinocyclohexanecarbonitrile

   a. RITCHIE, P. D., 1952 (99)

      $CH_2(CH_2)_4C(NHC_6H_5)CN \longrightarrow HCN + CH_2(CH_2)_4C{:}NC_6H_5$

      Temperature of 245° (reflux)

      Heated for 15 minutes.

6. α-Anilinohydratroponitrile

   a. RITCHIE, P. D., 1952 (99)

      $C_6H_5NHC(C_6H_5)(CH_3)CN \longrightarrow HCN + C_6H_5C(CH_3){:}NC_6H_5$

      Temperature of 210° (reflux)

      Heated for one hour.

C. Diamines

1. N^1,N^1-Diethyl-1,4-pentanediamine

   a. BALANDIN, A. A., and VASYUNINA, N. A., 1948 (5)

      $(C_2H_5)_2N(CH_2)_3CH(NH_2)CH_3 \longrightarrow H_2 + (C_2H_5)_2N(CH_2)_3C(CH_3){:}NH$

      Temperature of 254 to 323°

      Used Pd as catalyst.

b. BALANDIN, A. A., and VASYUNINA, N. A., 1955 (6)

$(C_2H_5)_2N(CH_2)_3CH(NH_2)CH_3 \longrightarrow$ dehydrogenation

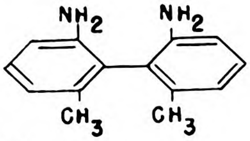
Temperature of 270 to 330°

With Pd-asbestos catalyst the rate constant varied from 9.4 to 23.87 min.^{-1} and the activation energy was 11,400 cal./mole.

With Ni on Al_2O_3 catalyst the rate constant varied from 9.06 to 28.6 min.^{-1} and the activation energy was 10,730 cal./mole.

2. 2, 2'Diamino-6, 6'dimethylbiphenyl

a. KISTIAKOWSKY, G. B., and SMITH, W. R., 1936 (57)



→ dimerization

The reaction was first-order and homogeneous

$k = 2.35 \times 10^{10} \text{ exp. } -(45,100/RT) \text{ sec.}^{-1}$

3. N, N'-Dinitroethylenediamine

a. ROBERTSON, A. J. B., 1948 (101)

Temperature of 184 to 254°

The reaction was first-order, $t_{1/2}$ at 184° = 43 sec., at 254° $t_{1/2}$ = 1/2 sec.

4. 2, 4, 6-Trinitrophenylmethylnitramine

a. ROBERTSON, A. J. B., 1948 (101)

Temperature of 184 to 254°

III. AMINO ACIDS

$[R(NH_2)COOH]$

A. Aliphatic amino acids

1. N, N-Diethyl-β-alanine

a. CLARKE, R. L., and MOORADIAN, A., 1949 (25)

$(C_2H_5)_2N(CH_2)_2COOH \rightarrow (C_2H_5)_2NH$ + residue

Temperature of 225 to 230°

Heating of the residue to 250° produced γ-butyrolactone and a basic oil.

2. 2-Aminohendecanoic acid

a. CHAMPETIER, G., and VERGOZ, R., 1950 (22)

$CH_3(CH_2)_8CH(NH_2)COOH \rightarrow$ loss of free NH_2 groups + polycondensation

Temperature of 213°

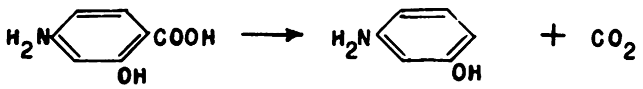
The reaction was not bimolecular.

The acid was fused in a stream of nitrogen.

B. Aromatic amino acids

1. p-Aminosalicyclic acid

a. SHEINKEV, Y. N., and PERSIYANOVA, I. V., 1953 (110)



Temperature of 60 to 100°

Activation energy of 20, 500 cal. /mole.

The reaction was catalyzed by water and m-aminophenol.

2. γ-Diethylamino-α-phenylbutyric acid

   a. CLARKE, R. L., and MOORADIAN, A., 1949 (25)

   $$(C_2H_5)_2N(CH_2)_2CH(C_6H_5)COOH \rightarrow \underline{CH_2CH_2CH(C_2H_5)COO}$$

   Temperature of 210 to 220°

   Heated for 30 minutes.

3. γ-Diethylamino-α-(2-diethylaminoethyl)-α-phenylbutyric acid

   a. CLARKE, R. L., and MOORADIAN, A., 1949 (25)

   $$C_6H_5C\left[CH_2CH_2N(C_2H_5)_2\right]_2COOH \rightarrow (C_2H_5)_2NH +$$
   $$\underline{CH_2CH_2C(C_6H_5)\left[CH_2CH_2N(C_2H_5)_2\right]COO}$$

   Temperature of 210 to 220°

   Heated for 30 minutes.

4. γ-Diethylamino-α,α-diphenylbutyric acid

   a. CLARKE, R. L., and MOORADIAN, A., 1949 (25)

   $$(C_2H_5)_2N(CH_2)_2C(C_6H_5)_2COOH \rightarrow CO_2 + (C_2H_5)_2NH +$$
   $$C_6H_5(CH_2)_3N(C_2H_5)_2 + \underline{CH_2CH_2C(C_6H_5)_2COO}$$

   Temperature of 210 to 220°

5. δ-Diethylamino-α,α-diphenylvaleric acid

   a. CLARKE, R. L., and MOORADIAN, A., 1949 (25)

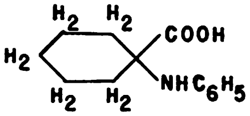
   $$(C_2H_5)_2N(CH_2)_3C(C_6H_5)_2COOH \rightarrow (C_6H_5)_2CH(CH_2)_3N(C_2H_5)_2 +$$
   $$CO_2$$

   Temperature of 200 to 250°

   Heated for one hour at 200° and then one hour at 250°.

6. 1-Anilinocyclohexanecarboxylic acid

   a. BAIN, W. C., and RITCHIE, P. D., 1955 (4)



$$\longrightarrow CO + CO_2 + H_2 + C_6H_6 + C_6H_{12}$$

Temperature of 500°

7. 3-Hydroxyamino-3-phenylpropionic acid

   a. BARGELLINI G., and TURI, C. J., 1954 (8)

$$C_6H_5CH(NHOH)CH_2COOH \longrightarrow CO_2 + NH_3 + C_6H_5CH_2CH_3 + C_6H_5CH{:}CHCOOH + \text{dark-red resin}$$

Temperature of 170°

IV. AMMONIA

[NH_3]

A. Unsubstituted

1. Ammonia

a. CHRISTIANSEN. J. A., and KNUTH, E., 1935 (24)

$NH_3 \rightleftharpoons NH + H_2$

$NH \rightleftharpoons NH^*$

$NH^* + NH_3 \rightleftharpoons N_2 + 2H_2$

Temperature of 789 to 859°

Final pressure of 36.50 to 5942 mm.

Work done in a quartz bulb of 200 cc. volume and 210 cm^2 area.

NH and NH* are two different forms of the same radical.

b. SZWARC, M., 1949 (124)

Studied the dissociation energy of the first N-H bond in ammonia. Pyrolysis of NH_3 proved unsuitable for the purpose.

c. RUSOV, M. T., and PEVZNER, TS. V., 1954 (103)

Temperature of 700 to 900°

Pressure of 100 mm.

Activation energy in the presence of SiO_2 above 720° was 38,200 cal./mole., with Cu it was 57,600 to 62,000 cal./mole. With Fe as catalyst the reaction took place above 740°.

B. Quaternary ammonium salts.

1. Allyltrimethylammonium hydroxide (Homoneurine)

a. HOWTON, D. R., 1949 (50)

$[CH_2{:}CHCH_2N(CH_3)_3]\,OH \longrightarrow (CH_3)_2NH + (CH_3)_3N + CH_2{:}CHCH_2OH +$
$C_2H_5CH{:}C(CH_3)CHO + CH_3C{\vdots}CH + CH_2{:}C{:}CH_2 +$ small
amounts of C_2H_5CHO and $CH_2{:}CHCH{:}CHCH{:}CH_2$

Temperature of 310 to 325°

The ratio of $(CH_3)_2NH$ to $(CH_3)_3N$ was 1:2.

b. LUKES, R., and TROJANEK, J., 1949 (71)

$[CH_2{:}CHCH_2N(CH_3)_3]\,OH \longrightarrow (CH_3)_2NH + (CH_3)_3N +$
$CH_2{:}C{:}CH_2 + CH_3C{\vdots}CH + C_2H_5CHO + C_2H_5CH{:}C(CH_3)CHO$

Temperature of 200°

2. *dl*-6-Dimethylamino-4, 4-diphenyl-3-heptanol methiodide (α-*dl*-Methadol methiodide)

a. EASTON, N. R., and FISH, V. B., 1955 (34)

α-*dl*-Methadol methiodide ⟶ 2-ethyl-3, 3-diphenyltetrahydrofuran

Temperature of open flame

Pressure of 15 to 20 mm

3. *dl*-6-Dimethylamino-5-methyl-4, 4-diphenyl-3-hexanol methiodide (α-*dl*-Isomethadol methiodide)

a. EASTON, N. R., and FISH, V. B., 1955 (34)

α-*dl*-Isomethadol methiodide ⟶ α-*dl*-5-methyl-2-ethyl-3, 3-diphenyltetrahydrofuran

Temperature of open flame

Pressure of 15 to 20 mm

4. *d*-6-Dimethylamino-5-methyl-4, 4-diphenyl-3-hexanol methiodide (α-*d*-Isomethadol methiodide)

   a. EASTON, N. R., and FISH, V. B., 1955 (*34*)

      α-*d*-Isomethadol methiodide ⟶ α-*dl*-4-methyl-2-ethyl-3, 3-diphenyltetrahydrofuran

      Temperature of open flame

      Pressure of 15 to 20 mm

5. *l*-6-Dimethylamino-5-methyl-4, 4-diphenyl-3-hexanol methiodide (α-*l*-Isomethadol methiodide)

   a. EASTON, N. R., and FISH, V. B., 1955 (*34*)

      α-*l*-Isomethadol methiodide ⟶ α-*d*-4-methyl-2-ethyl-3, 3-diphenyltetrahydrofuran

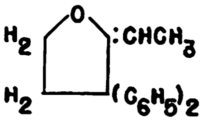
      Temperature of open flame

      Pressure of 15 to 20 mm

6. 6-Dimethylamino-4, 4-diphenyl-3-hexanone methiodide

   a. EASTON, N. R., NELSON, S. J., FISH, V. B., and CRAIG, P. N., 1953 (*35*)

      $(CH_3)_2NCH_2CH_2C(C_6H_5)_2COC_2H_5 \cdot CH_3I \rightarrow$



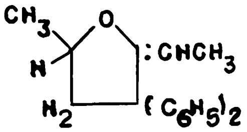
      Temperature of open flame

      Pressure of 15 mm

7. 6-Dimethylamino-4, 4-diphenyl-3-heptanone methiodide

   a. EASTON, N. R., NELSON, S. J., FISH, V. B., and CRAIG, P. N., 1953 (*35*)

      $(CH_3)_2NCH(CH_3)CH_2C(C_6H_5)_2COC_2H_5 \cdot CH_3I \rightarrow$



Temperature of open flame

Pressure of 15 mm.

8. Arylamine salts

a. KATO, S., and SOMENO, F., 1939 (56)

ArNHR + HX $\longrightarrow$ quinquavalent N salt

Quinquavalent N salt $\longrightarrow$ trivalent amine salt + RX

Trivalent amine salt + RX $\longrightarrow$ quinquavalent NH_4 salt

Quinquavalent NH_4 salt $\longrightarrow$ $R\text{-}Ar\text{-}NH_2$ (o- or p-)

All reactions after the first reaction are thermal. The second reaction is above the melting point of the salt. The last reaction is a thermal decomposition.

V. AZIDES

[RN_3]

A. Aliphatic azides

1. General

a. YOFFE, A. D., 1951 (148)

Some organic azides melt before explosion.

Nitrogen is the main product during decomposition.

2. Methyl azide

a. LEERMAKERS, J. A., 1933 (66)

$$CH_3N_3 \longrightarrow (CH_2)_6N_4 + NH_3 + HN_3 + C_2H_6 + C_2H_4$$

Temperature of 200°

The reaction was first-order and at high pressures

$$k = 3.02 \times 10^{15} \text{ exp. } -(43,500/RT) \text{ sec.}^{-1}$$

The reaction rate decreased at pressures below 10 cm.

3. Ethyl azide

a. LEERMAKERS, J. A., 1933 (65)

Temperature of 199.4 to 239.6°

Pressure of 20 to 195 mm.

The reaction was unimolecular,

$$k = 2.06 \times 10^{14} \text{ exp. } -(39,740/RT) \text{ sec.}^{-1}$$

Below 20 mm. pressure, the rate decreased with decreasing pressure.

b. CAMPBELL, H. C., and RICE, O. K., 1935 (19)

Studied the critical explosion pressure.

The critical explosion pressure varied from 105.2 mm. at 258.5° to 3.1 mm. at 320.2°

Carbon dioxide had no effect while helium appreciably raised the critical pressure.

B. Aromatic azides

1. General

a. YOFFE, A. D., 1951 (148)

Some organic azides melt before explosion.

During decomposition, nitrogen is the main product.

2. Benzoylazide

a. PORTER, C. W., and YOUNG, L., 1938 (91)

$C_6H_5CON_3 \longrightarrow N_2 + C_6H_5NCO$

3. 4'-Hydroxy-2-azidoacetophenone

a. BOYER, J. H., and STRAW, D., 1953 (16)

4'-Hydroxy-2-azidoacetphenone ⟶ 2-Hydroxybenzoyl-5-(hydroxyphenyl)imidazole

4. 2'Amino-2-azidoacetophenone

a. BOYER, J. H., and STRAW, D., 1953 (16)

2'-Amino-2-azidoacetophenone ⟶ indigo

VI. AZINES

[RCH:NN:CHR]

A. Aromatic Azines

1. Benzaldazine

a. WILLIAMS, G., and LAWRENCE, A. S. C., 1936 (145)

$C_6H_5CH{:}NN{:}CHC_6H_5 \longrightarrow N_2 + C_6H_5CH{:}CHC_6H_5$ (75% yield)

Temperature of 318 to 354°

Pressure of 5 to 380 mm.

The reaction was first-order and homogeneous,

$k = 2.25 \times 10^{16} \text{ exp. } -(53,000/RT) \text{ sec.}^{-1}$

2. Benzalfluorenoneazine

a. HOWARD, L. B., HILBERT, G. E., and GADDY, V. L., 1932 (49)

Benzalfluorenoneazine → 9-iminofluorene

3. Anisaldazine

a. HOWARD, L. B., HILBERT, G. E., and GADDY, V. L., 1932 (49)

There was little effect on the reaction from 100 atm. of hydrogen or nitrogen pressure.

4. p-Tolualdazine

a. HOWARD, L. B., HILBERT, G. E., and GADDY, V. L., 1932 (49)

p-Tolualdazine → 2, 4, 5-triphenylimidazole

5. Benzophenoneazine

a. HOWARD, L. B., HILBERT, G. E., and GADDY, V. L., 1932 (49)

$(C_6H_5)_2C{:}NN{:}C(C_6H_5)_2 \longrightarrow C_6H_5CN$

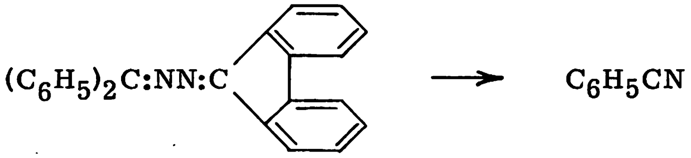
6. Acetophenoneazine

   a. HOWARD, L. B., HILBERT, G. E., and GADDY, V. L., 1932 (49)

   $C_6H_5C(CH_3){:}NN{:}C(CH_3)C_6H_5 \longrightarrow C_6H_5CN$

7. Fluorenonbenzophenoneazine

   a. HOWARD, L. B., HILBERT, G. E., and GADDY, V. L., 1932 (49)



VII. AZO COMPOUNDS

[RN:NR]

A. Aliphatic azo compounds

1. Azomethane

a. RAMSPERGER, H. C., 1930 (93)

The reaction was first-order in the presence of added ethane.

Added nitrogen had little effect.

b. STEACIE, E. W. R., 1931 (114)

$CH_3N{:}NCH_3 \longrightarrow N_2 + C_2H_4$

Bimolecular, homogeneous reaction with an approximate activation energy of 36,000 cal./mole.

c. LEERMAKERS, J. A., 1933 (67)

Temperature above 475°

A cold Pd mirror, 10 cm. from the furnace, was removed. This indicated the production of methyl radicals.

d. HEIDT, L. J., and FORBES, G. S., 1935 (45)

$CH_3N{:}NCH_3 \longrightarrow N_2 + CH_4$ (An assumed reaction)

Temperature of 300°

The reaction was first-order.

Work was done in a quartz tube.

The reaction was measured by pressure increase.

e. RICE, O. K., and SICKMAN, D. V., 1936 (98)

Unimolecular chain reaction with short chains.

Helium activated the decomposition.

Chain length was independent of temperature and pressure.

f. SICKMAN, D. V., and RICE, O. K., 1936 (112)

Description of apparatus used for measuring the reaction rate in the presence of a large excess of inert gas.

g. SICKMAN, D. V., and RICE, O. K., 1936 (113)

Studied the effects of added gases.

h. RIBLETT, E. W., and RUBIN, L. C., 1937 (95)

$CH_3N{:}NCH_3 \longrightarrow N_2 + CH_4 + C_2H_6 +$ higher molecular weight compounds containing nitrogen

Temperature of 340°

The reaction was first-order.

The reaction rate constant was measured by product analysis and was 50% greater than that by pressure increase.

i. TAYLOR, H. A., and JAHN, F. P., 1939 (134)

$CH_3N{:}NCH_3 \longrightarrow (CH_3)_2N{:}N(CH_3)_2 \longrightarrow$ decomposition products

Temperature of 290 to 340°

Activation energy of 52, 500 cal. /mole.

The mole ratio of products to reactants was 1. 95 at 50% reaction.

j. JAHN, F. P., and TAYLOR, H. A., 1939 (52)

Added nitric oxide.

No initial inhibition.

Products were nitrogen and methane.

Activation energy was 52, 500 cal. /mole.

The nitric oxide did not completely stop the addition of methyl radicals to the $CH_3N{:}NCH_3$.

$CH_3^{\cdot} + NO \longrightarrow CH_2NOH$, was partially oxidized by nitric oxide.

k. PAGE, M., PRITCHARD, H. O., and TROTMAN-DICKENSON, A. F., 1953 (84)

$CH_3N{:}NCH_3 \longrightarrow CH_4 + C_2H_6 + N_2$

Temperature of 390 to 450°

Pressure of 15 mm.

The reaction was first order,

$k = 10^{14}$ exp. $-(46,000/RT)$ sec.$^{-1}$, k was pressure dependent.

The reaction was studied by the flow method using toluene as a carrier gas. The first step of the reaction was splitting off of methyl radicals.

2. 1, 1'-Dimethylazoethane

a. RICE, F. O., and EVERING, B. L., 1933 (96)

Temperature of 450 to 500°

The reaction was performed in the presence of acetone.

Isopropyl radicals were not found.

3. Azodi-isobutyronitrile

a. ZEIGLER, K., DEPARADE, W., and MEYE, W., 1950 (149)

$(CH_3)_2C(CN)N{:}NC(CN)(CH_3)_2 \longrightarrow [(CH_3)_2\dot{C}\,CN] \longrightarrow$ decomposition products

The reaction was first-order.

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B. Aromatic azo compounds

1. ω-Azotoluene

a. WILLIAMS, G., and LAWRENCE, A. S. C., 1936 (146)

$C_6H_5CH_2N{:}NCH_2C_6H_5 \longrightarrow N_2 + (C_6H_5)_2$

Temperature of 187 to 238°

Pressure of 2.5 to 11 mm.

The reaction was first-order and homogeneous with an activation energy of 35,000 cal./mole.

More energy was required to break the C:N bond in azines than to break the C-N bond in azo compounds.

2. α,α'-Azobis[α-methyl] hydrocinnamonitrile

a. OVERBERGER, C. G., and BILETCH, H., 1951 (83)

$C_6H_5CH_2C(CN)(CH_3)N{:}NC(CN)(CH_3)CH_2C_6H_5 \longrightarrow$

$C_6H_5C(CN)(CH_3)C(CN)(CH_3)C_6H_5$

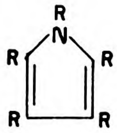
Temperature of 100°

Heated for five hours.

The p-chloro- derivative reacted in a similar manner.

VIII. HETEROCYCLIC NITROGEN COMPOUNDS

A. Pyrroles



1. General

   a. ODDO, B., 1939 (81)

      A literature review and discussion.

2. 1-(2-Pyridyl)pyrrole

   a. OOSTERHUIS, A. G., and WIBAUT, J. P., 1936 (82)

      1-(2-Pyridyl)pyrrole ⟶ 2-(2-pyridyl)pyrrole + 3-(2-pyridyl)-pyrrole

      Temperature of 710°

      Flow rate of 2.1 ml./min.

      Used pumice as a catalyst.

      The products contained 50% of the 2-isomer and 10% of the 3-isomer.

3. 3-(2-Pyridyl)pyrrole

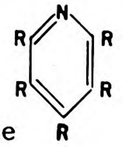
   a. OOSTERHUIS, A. G., and WIBAUT, J. P., 1936 (82)

      3-(2-Pyridyl)pyrrole ⟶ 2-(2-pyridyl)pyrrole

      Temperature of 710°

      Used pumice as a catalyst.

B. Pyridines



1. Pyridine

a. PLOQUIN, J., 1947 (88)

Pyridine → acetylenic hydrocarbons + piperidine + pyrrole + indole + H_2 + CH_3NH_2 + NH_3 + NH_4CN + C

Temperature of 350 to 550°

Used Al_2O_3 as catalyst.

Proposed mechanisms:

Pyridine → biactylene + CH_3NH_2

Biacetylene + NH_3 → pyrrole

Pyrrole + biacetylene → indole

Pyridine + 2biacetylene → acridine

Pyridine + H → CH_2:NCH:CHCH:CH_2 → 1-methylpyrrole

Pyridine + H → HN:CHCH:CHCH:CH_2 → 2-methylpyrrole

methylpyrrole → pyrrole + CH_4

Gas carbon had no catalytic effect.

b. KRUMHOLZ, P., 1949 (60)

Pyridine → bipyridyl + indole + other compounds

Temperature of 850 to 870°

All possible bipyridyls are formed.

2. Methylpyridines

a. ROBERTS, J. S., and SZWARC, M., 1948 (100)

Methylpyridines → bipicolyls

Temperature of 780 to 823°

Pressure of "a few millimeters"

The reaction was free-radical. The rate determining step was the formation of H$^{\bullet}$ and picolyl radicals.

The reaction was studied by the flow method using toluene as a carrier gas.

Methyl group C-H bond energies were calculated for the three methylpyridines.

3. 2, 4-Dimethylpyridine

   a. GRANELLI, C., 1937 (40)

      Temperature of 250°

      Used nickel as a catalyst.

4. Pyridine 1-oxide

   a. KATADA, M., 1947 (55)

      Pyridine 1-oxide → pyridine

      The oxide decomposed at 210 to 230°.

      Added copper dust lowered the initial decomposition temperature to 140°, added zinc dust lowered it to 170° and added phenyl nitrate and copper dust lowered it to 180°.

      The decomposition temperatures were determined by visual change.

5. 1-(2-Pyridyl)pyrrole

   a. OOSTERHUIS, A. G., and WIBAUT, J. P., 1936 (82)

      1-(2-Pyridyl)pyrrole → 2-(2-pyridyl)pyrrole + 3-(2-pyridyl)pyrrole

      Temperature of 710°

Flow rate of 2.1 ml./min.

Used pumice as a catalyst.

The products contained 50% of the 2-isomer and 10% of the 3-isomer.

6. 3-(2-Pyridyl)pyrrole

a. OOSTERHUIS, A. G., and WIBAUT, J. P., 1936 (82)

3-(2-Pyridyl)pyrrole ⟶ 2-(2-pyridyl)pyrrole

Temperature of 710°

Used pumice as a catalyst.

7. 2-(3-Pyridyl)piperidine (Anabasine)

a. DUBININ, B. M., and CHENINTSEV, G. V., 1946 (32)

2-(3-Pyridyl)piperidine ⟶ pyridine + 2-methylpyridine + 2-ethylpyridine + 2,3'-bipyridyl + 5-methylisoquinoline + $HCN + NH_3$

Temperature of 580 to 650°

Used charcoal as catalyst.

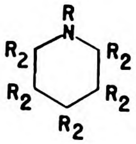
8. Dipyridinium halide salts

a. LYLE, R. E., and GARDIKES, J. J., 1955 (72)

Dipyridinium salt of $(CH_2CH_2Br)_2 \longrightarrow$ pyridine.HBr + $(CH_2BrCHBr)_2$

Dipyridinium salt of $Br(CH_2)_5Br \longrightarrow$ pyridine.HBr + $CH_2{:}CHCH{:}CHCH_3$

Temperature of 230 to 270°

C. Piperidines 

1. 2-(3-Pyridyl)piperidine (Anabasine)

a. DUBININ, B. M., and CHENINTSEV, G. V., 1946 (32)

2-(3-Pyridyl)piperidine ⟶ pyridine + 2-methylpyridine + 2-ethylpyridine + 2, 3'-bipyridyl + 5-methylisoquinoline + HCN + NH_3

Temperature of 580 to 650°

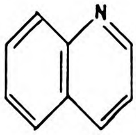
Used charcoal as catalyst.

2. 1, 1, 1-Tripiperidinoethane

a. McELVAIN, S. M., and TATE, B. E., 1945 (74)

1, 1, 1-Tripiperidinoethane ⟶ piperidine + polymeric material

Temperature of 290 to 300° (Reflux temperature)

D. Quinolines 

1. Quinoline 1-oxide

a. KATADA, M., 1947 (55)

Quinoline 1-oxide ⟶ quinoline

Temperature of 160°

Decomposition was incomplete. Decomposition temperature was not changed by the addition of Cu dust, Zn dust or phenylnitrate.

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2. 4-Ethoxyquinoline 1-oxide

a. KATADA, M., 1947 (55)

4-Ethoxyquinoline 1-oxide ⟶ 4-ethoxyquinoline

Temperature of 150 to 200°

The decomposition was incomplete. Decomposition temperature was not changed by the addition of Cu dust, Zn dust or phenylnitrate.

3. 4-Nitroquinoline 1-oxide

a. KATADA, M., 1947 (55)

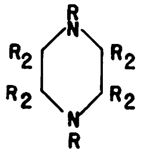
4-Nitroquinoline 1-oxide ⟶ 4-nitroquinoline

Temperature of 152° (Melting point)

The compound fused and the products carbonized.

There was no change in decomposition temperature with the addition of Cu dust, Zn dust or phenylnitrate.

E. Piperazines



1. 1, 1, 4, 4-Tetraalkylpiperazinium dichlorides

a. CADOGEN, J. I. G., 1955 (18)

1, 1, 4, 4-Tetraalkylpiperazinium dichlorides ⟶ 1, 4-dialkylpiperazine + alkyl chloride

Atmospheric pressure

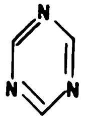
2. 1, 1, 4, 4-Tetraalkylpiperazinium dibromides

   a. CADOGEN, J. I. G., 1955 (18)

   1, 1, 4, 4-Tetraalkylpiperazinium dibromides ⟶ 1, 4-dialkylpiperazine + alkyl bromide

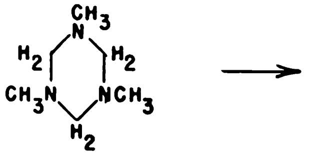
   Atmospheric pressure

F. s-Triazines



1. Hexahydro-1, 3, 5-trimethyl-s-triazine

   a. ANDERSON, J. L., 1956P (2)



$CH_3N{:}CH_2$

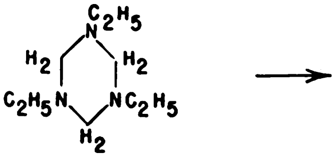
   Temperature of 425 to 450°

   Pressure below 10^{-4} mm.

   Used alumina-silica catalyst.

2. Hexahydro-1, 3, 5-triethyl-s-triazine

   a. ANDERSON, J. L., 1956P (2)



$C_2H_5N{:}CH_2$

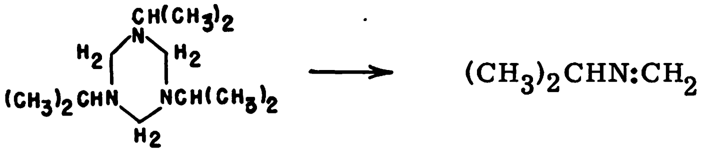
   Temperature of 425 to 450°

   Pressure below 10^{-4} mm.

   Used alumina-silica catalyst.

3. Hexahydro-1, 3, 5-triisopropyl-s-triazine

   a. ANDERSON, J. L., 1956P (2)



Temperature of 425 to 450°

Pressure below 10^{-4} mm.

Used alumina-silica catalyst.

4. Hexhydro-1, 3, 5-triisopentyl-s-triazine

   a. ANDERSON, J. L., 1956P (2)

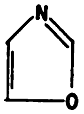
Hexahydro-1, 3, 5-triisopentyl-s-triazine → iso-$C_5H_{11}N{:}CH_2$

Temperature of 425 to 450°

Pressure of 10^{-4} mm.

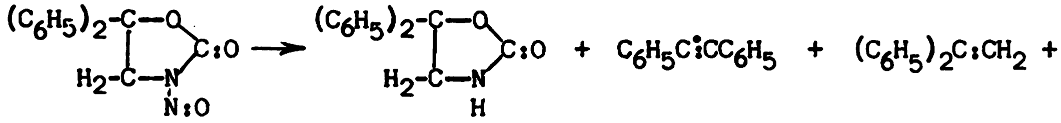
Used alumina-silica catalyst.

G. Oxazoles



1. 3-Nitroso-5, 5-diphenyl-2-oxazolidone

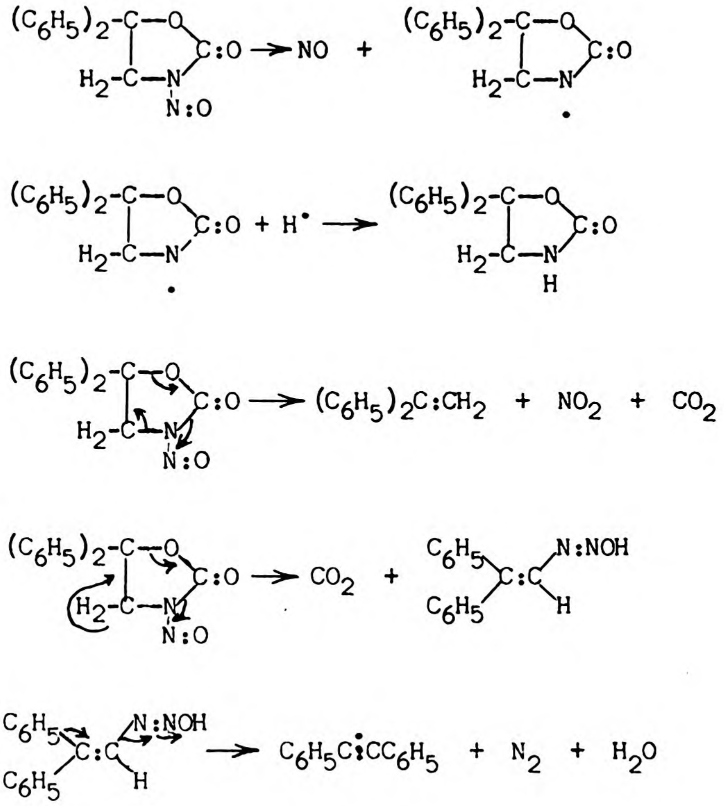
   a. NEWMAN, M. S., and WEINBERG, A. E., 1957 (79)



$C_6H_5OC_6H_5 + H_2O + NO + N_2 + N_2O + CO_2 +$ residue

Temperature of 120 to 185°

Proposed mechanisms:



The second reaction was favored at low temperatures.

2. 3-Nitroso-5-methyl-5-phenyl-2-oxazolidone

   a. NEWMAN, M. S., and WEINBERG, A. E., 1957 (79)

   (No data given.)

3. 3-Nitroso-1-oxazolspiro(4, 5)decane-2-one

   a. NEWMAN, M. S., and WEINBERG, A. E., 1957 (79)

   (No data given.)

IX. HYDRAZINES

$$\begin{bmatrix} RNHNHR \\ R_2NNR_2 \end{bmatrix}$$

A. Aliphatic hydrazines

1. Hydrazine

a. SZWARC, M., 1949 (124)

$N_2H_4 \longrightarrow 2NH_2^{\cdot}$

$NH_2^{\cdot} \longrightarrow H_2 + N_2 + NH_3$

The first reaction is a first-order, homogeneous reaction,

$k = 4 \times 10^{12} \text{ exp. } -(60,000 \pm 3,000)/RT \text{ sec.}^{-1}$

The second reaction is heterogeneous.

The reaction was studied by the flow method using toluene as a carrier gas.

At 600°, only 2% of the total decomposition was homogeneous, at 780°, about 30% of the decomposition was homogeneous.

b. SZWARC, M., 1949 (125)

$3N_2H_4 \longrightarrow N_2 + 4NH_3$

$2N_2H_4 \longrightarrow H_2 + N_2 + 2NH_3$

$N_2H_4 \longrightarrow 2NH_2^{\cdot}$

Temperature of 630 to 780°

Pressure of "a few millimeters"

The first two reactions were heterogeneous and the third reaction was homogeneous and first-order.

2. 1,2-Diethylhydrazine

a. TAYLOR, H. A., and DITMAN, J. G., 1936 (132)

$$C_2H_5NHNHC_2H_5 \longrightarrow N_2 + H_2 + 2C_2H_5^{\cdot}$$

$$2C_2H_5^{\cdot} \longrightarrow CH_4 + C_4H_{10} + \text{unsaturated hydrocarbons}$$

This was a first-order chain reaction.

B. Aromatic hydrazines

1. Triphenylhydrazine

a. HOLT, P. F., and HUCHES, B. P., 1955 (48)

Triphenylhydrazine-1-N^{15}

The products contained azobenzene with random nitrogen-15 distribution.

X. NITRATES

$[RONO_2]$

A. Aliphatic Nitrates

1. General

a. PHILLIPS, L., 1950 (86)

Proposed mechanisms:

$$RCH_2ONO_2 \rightleftharpoons RCH_2O^{\cdot} + NO_2$$

$$RCH_2O^{\cdot} + RCH_2ONO_2 \longrightarrow RCHO + NO_2$$

2. Methyl nitrate

a. APPIN, A., TODES, O., and KHARITO, Y., 1936 (3)

$$2CH_3ONO_2 \longrightarrow CH_2O + CH_3OH + 2NO_2$$

Temperature of 210 to 240°

Pressure of 5 to 15 mm.

The reaction was unimolecular,

$$k = 2.5 \times 10^{14} \text{ exp. } -(39,500/RT) \text{ sec.}^{-1}$$

The reaction exhibited an induction period.

At temperatures of 256 to 374°, the nitrate exploded.

Proposed reaction for the explosion:

$$2CH_3ONO_2 \longrightarrow 2CH_2O + H_2O + NO_2 + NO$$

$$2CH_3ONO_2 \longrightarrow CH_2O + 2H_2O + CO + 2NO$$

b. GRAY, P., and YOFFE, A. D., 1949 (41)

The explosion of methyl nitrate was not a true thermal reaction but a chain-branching reaction.

c. GRAY, P., and YOFFE, A. D., 1949 (42)

Temperature of 240 to 500°

Determined the critical explosion pressure.

Argon, nitrogen, and oxygen facilitated the explosion.

Used a quartz container.

3. Ethyl nitrate

a. THEILE, H., 1948 (137)

$$C_2H_5ONO_2 \longrightarrow CH_2O + C_2H_5NO_2 + H_2O + CO + H_2 + NO_2$$

Temperature of 200 to 250°

Partial pressure of 16 mm. of sample in a nitrogen carrier gas.

The reaction was first-order with an activation energy of 32,000 ± 5,000 cal./mole.

Proposed mechanisms:

$$C_2H_5ONO_2 \longrightarrow C_2H_5O^{\cdot} + NO_2$$

$$C_2H_5O^{\cdot} \longrightarrow CH_3^{\cdot} + CH_2O$$

$$CH_3^{\cdot} + C_2H_5ONO_2 \longrightarrow CH_3O^{\cdot} + C_2H_5NO_2$$

$$CH_3O^{\cdot} + C_2H_5ONO_2 \longrightarrow CH_3O_2^{\cdot} + C_2H_5NO_2$$

$$CH_3O_2^{\cdot} \longrightarrow CH_2O + HO^{\cdot}$$

$$CH_3O^{\cdot} + HO^{\cdot} \longrightarrow CH_2O + H_2O$$

$$CH_2O \longrightarrow CO + H_2$$

b. ADAMS, G. K., and BAWN, C. E. H., 1949 (1)

$$C_2H_5ONO_2 \longrightarrow C_2H_5O^{\cdot} + NO_2$$

$$C_2H_5O^{\cdot} \longrightarrow C_2H_4O$$

$C_2H_4O + NO_2 \longrightarrow NO + CO + CO_2$

Temperature of 180 to 215°

The reaction was first-order, $k = 10^{15.8} \exp. -(39,900/RT) \text{ sec.}^{-1}$

c. GRAY, P., and YOFFE, A. D., 1949 (42)

Temperature of 240 to 500°

Determined the critical explosion pressure.

Argon, nitrogen and oxygen facilitated the explosion.

Used a quartz vessel.

d. POLLARD, F. H., WYATT, R. M. H., and MARSHALL, H. S. B., 1950 (90)

Added NO_2

Decomposition was retarded up to a certain concentration of NO_2. Above this concentration the decomposition was increased.

e. POLLARD, F. H., MARSHALL, H. S. B., and PEDLER, A. E., 1956 (89)

$C_2H_5ONO_2 \longrightarrow CO_2 + CO + NO + N_2O + N_2 +$

$C_2H_5NO_2 +$ trace of H_2

Temperature of 175 to 209°

The reaction was first-order,

$k = 10^{14.74} \exp. -(38,000 \pm 380)/RT \text{ sec.}^{-1}$

4. Nitrocellulose

a. LAMBREY, M., 1934 (63)

Nitrocellulose ⟶ nitric oxide + decomposition products

Temperature of 43°

The reaction was measured by nitric oxide evolution which was 0.65×10^{-6} g./kg./day.

b. PHILLIPS, R. W., ORLICK, C. A., and STEINBERGER, R., 1955 (87)

Thin film (3 to 5 microns) decomposition.

Pressure below 100 mm.

The reaction was first-order, $k = 3.54 \times 10^{8} \exp. -(45,000/RT) \sec.^{-1}$

The amount of reaction was determined by infrared analysis (monitored to the nitric oxide peak).

The carbon skeleton was not changed.

c. WOLFROM, M. L., FRAZER, J. H., JUHN, L. P., DICKEY, E. E., OLIN, S. M., HOFFMAN, D. O., BOWER, R. S., CHANEY, A., CARPENTER, E., and McWAIN, P., 1955 (147)

Propellant cellulose nitrate decomposition

Ignition conditions (hot wire).

Pressure of 2 to 3 mm.

5. Tetranitropentaerythritol

a. LAMBREY, M., 1934 (63)

Tetranitropentaerythritol ⟶ nitric oxide + decomposition products

Temperature of 43°

The nitric oxide evolution was just measurable.

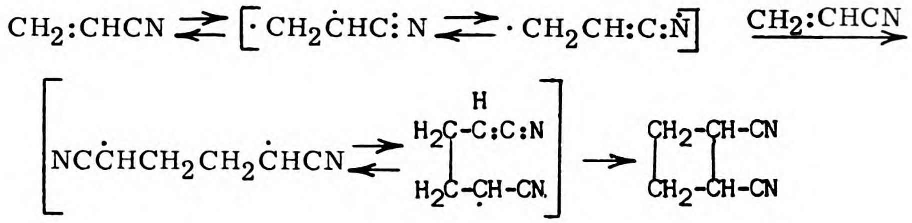
XI. NITRILES

[RCN]

A. Aliphatic nitriles

1. Acrylonitrile

a. COYNER, E. C., and HILLMAN, W. S., 1949 (30)



2. Azoisobutyronitrile

a. ZEIGLER, K., DEPARADE, W., and MEYE, W., 1950 (149)

$(CH_3)_2C(CN)N{:}NC(CN)(CH_3)_2 \longrightarrow [(CH_3)_2\dot{C}CN] \longrightarrow$ decomposition products

First-order reaction.

3. Hydroxynitriles

a. BEACH, L. K., 1948P (9)

R(OH)CR'R''CN → alkylcyanide + aldehyde or ketone

R = alkylene or alkylidene, R' and R'' = hydrogen or alkyl.

Temperature of 487°

Used pumice as catalyst.

Residence time of 2.8 seconds.

b. DVORAK, J., 1951 (33)

Acetylated hydroxyacidnitrile yielded the ethylenic nitriles.

Increased molecular weight permitted easier pyrolysis.

4. Hydracrylonitrile

a. BEACH, L. K., 1948P (9)

$HOCH_2CH_2CN \longrightarrow CH_3CN$ (49% yield) + CH_2O

Temperature of 487°

Used pumice as catalyst.

Residence time of 2.8 seconds.

5. 2-Acetoxyisovaleronitrile

a. JOURNEAY, G. E., 1956 (54)

$CH_3(CH_2)_2CH(OCOCH_3)CN \longrightarrow (CH_3)_2C{:}CHCN$

Temperature of 600 ± 10°

Yield of 90%.

B. Aromatic nitriles

1. Styrene nitrile

a. KISTIAKOWSKY, G. B., and SMITH, W. R., 1936 (58)

$\underline{trans}\text{-}C_6H_5CH{:}CHCN \longrightarrow \underline{cis}\text{-}C_6H_5CH{:}CHCN$

Temperature of 308 to 377°

Pressure of about 400 mm.

The reaction was first-order and homogeneous,

$$k = 10^{11.6 \pm 0.4} \exp. -(46,000 \pm 1,000)/RT \text{ sec.}^{-1}$$

At low pressures, k increased due to wall reactions.

At 352° the equilibrium was 37% *cis*.

The equilibrium composition was practically independent of temperature.

2. α-Anilinohydratroponitrile

   a. RITCHIE, P. D., 1952 (99)

   $\mathrm{C_6H_5NHC(C_6H_5)(CH_3)CN \longrightarrow HCN + C_6H_5C(CH_3){:}NC_6H_5}$

   Temperature of 210° (reflux)

   Heated for one hour.

3. 1-Anilinocyclohexanecarbonitrile

   a. RITCHIE, P. D., 1952 (99)

   $\underbrace{\mathrm{CH_2(CH_2)_4C}}\mathrm{(NHC_6H_5)CN \longrightarrow HCN +} \underbrace{\mathrm{CH_2(CH_2)_4C}}\mathrm{{:}NC_6H_5}$

   Temperature of 245° (reflux)

   Heated for 15 minutes.

4. α,α-Azobis [α-methyl] hydrocinnamonitrile

   a. OVERBERGER, C. G., and BILETCH, H., 1951 (83)

   $\mathrm{C_6H_5CH_2C(CN)(CH_3)N{:}NC(CN)(CH_3)CH_2C_6H_5 \longrightarrow}$

   $\mathrm{C_6H_5C(CN)(CH_3)C(CN)(CH_3)C_6H_5}$

   Temperature of 100°

   Heated for five hours.

   The p-chloro- derivative reacted in a similar manner.

XII. NITRITES

[RONO]

A. Aliphatic nitrites

1. General

a. STEACIE, E. W. R., and ROSENBERG, S., 1936 (118)

General discussion.

2. Methyl nitrite

a. STEACIE, E. W. R., and SHAW, G. T., 1934 (119)

$CH_3ONO \longrightarrow NO + HCHO + CH_3OH$

Temperature of 190 to 240°

Initial prèssure of 50 to 490 mm.

The reaction was first-order and homogeneous,

$k = 1.84 \times 10^{13} \exp. -(36,400/RT) \text{ sec.}^{-1}$

The reaction constant was constant down to a pressure of 50 mm.

The reaction was measured by pressure increase.

b. STEACIE, E. W. R., and CALDER, D. S., 1936 (115)

Temperature of 210 to 240°

Pressure of 0.5 to 50 mm.

The reaction was unimolecular and heterogeneous.

The reaction was not a chain reaction and k decreased with decrease in pressure.

c. STEACIE, E. W. R., KATZ, S., ROSENBERG, A. L., and SMITH, W. McF., 1936 (117)

Temperature of 217.5°

Pressure of 650 mm. to 35 atmospheres

The decomposition rate was constant, indicating a unimolecular reaction.

d. CARTER, A. G., and TRAVERS, M. W., 1937 (21)

Temperature of 200°

The reaction was not unimolecular.

Work done in quartz.

3. Ethyl nitrite

a. LEVY, J. B., 1953 (68)

At high pressure:

$$C_2H_5ONO \longrightarrow C_2H_5O^{\cdot} + NO$$

$$C_2H_5O^{\cdot} \longrightarrow C_2H_5OH + CH_3CHO$$

At low pressure:

$$C_2H_5ONO \longrightarrow C_2H_5O^{\cdot} + NO$$

$$C_2H_5O^{\cdot} \longrightarrow CH_3^{\cdot} + CH_2O$$

$$2CH_3^{\cdot} \longrightarrow C_2H_6$$

Temperature of 181°

b. STEACIE, E. W. R., KATZ, S., ROSENBERG, A. L., and SMITH, W. McF., 1936 (117)

$$C_2H_5ONO \longrightarrow NO + CH_3CHO + C_2H_5OH$$

Temperature of 190 to 240°

Pressure above 50 mm.

The reaction was first-order and homogeneous,

$k = 1.39 \times 10^{14} \exp. -(37,700/RT) \text{ sec.}^{-1}$

The reaction was measured by pressure increase.

c. RICE, F. O., and RODOWSKAS, E. L., 1935 (97)

Activation energy for the primary dissociation of C_2H_5ONO was 34,300 ± 3,000 cal./mole.

At low pressures the reaction had no effect on cold metallic mirrors.

Temperature of 425° and dilution with an inert gas caused rapid mirror removal.

d. STEACIE, E. W. R., and KATZ, S., 1937 (116)

Discussion of theory of low-pressure work.

e. LEVY, J. B., 1956 (70)

$C_2H_5ONO \longrightarrow CH_3CHO + NO + C_2H_5OH + N_2O + H_2O$

Temperatures of 161, 181, and 201°

Pressures of 10 to 50 mm.

The reaction was a first-order reaction,

$k = 6.1 \times 10^{13} \exp. -(37,500 \pm 500)/RT \text{ sec.}^{-1}$

Studied the effects of added NO, CH_3CHO and C_2H_5OH.

Addition of large amounts of NO did not affect the reaction rate but increased CH_3CHO yield from 60 to 100% and N_2O from 20 to 50%. In the presence of added CH_3CHO, the rate increased sharply and no N_2O was formed.

Products were analyzed by infrared spectroscopy.

Proposed mechanisms:

$$C_2H_5ONO \rightarrow C_2H_5O^{\cdot} + NO$$

$$C_2H_5O^{\cdot} + NO \rightarrow NOH + CH_3CHO$$

$$2NOH \rightarrow N_2O + H_2O$$

$$C_2H_5^{\cdot} + NOH \rightarrow C_2H_5OH + NO$$

4. Propyl nitrite

a. STEACIE, E. W. R., and SHAW, G. T., 1935 (121)

$$C_3H_7ONO \rightarrow NO + C_2H_5CHO + C_3H_7OH$$

Temperature of 170 to 210°

The reaction was first-order and homogeneous,

$$k = 2.75 \times 10^{14} \text{ exp. } -(37,650/RT) \text{ sec.}^{-1}$$

b. STEACIE, E. W. R., and KATZ, S., 1937 (116)

Discussion of low pressure results.

c. LEVY, J. B., 1956 (69)

$$C_3H_7ONO \rightarrow C_3H_7OH + HCHO + NO + C_2H_5NO_2$$

Temperature of 181°

The reaction was measured by infrared analysis.

When NO was added, NO_2 became a product.

The presence of $C_2H_5NO_2$ in the products was questionable.

d. NAGIEV, M. F., PETROVA, Z. G., and SULTANOVA, A. I., 1956 (78)

$$2C_3H_7ONO \rightarrow 2NO + C_2H_5CHO + C_3H_7OH$$

Temperature of 200.0 to 229.75°

The reaction was first-order and homogeneous,

$k = 1.6 \times 10^{13} \exp. -(34,700/RT) \text{ sec.}^{-1}$

The reaction was measured by pressure change at constant volume and temperature.

5. Isopropyl nitrite

a. STEACIE, E. W. R., and SHAW, G. T., 1935 (122)

$2(CH_3)_2CHONO \longrightarrow 2NO + (CH_3)_2CO + (CH_3)_2CHOH$

Temperature of 170 to 210°

The reaction was first-order and homogeneous,

$k = 1.26 \times 10^{14} \exp. -(37,000/RT) \text{ sec.}^{-1}$

b. LEVY, J. B., 1956 (69)

$(CH_3)_2CHONO \longrightarrow (CH_3)_2CO + CH_3CHO + (CH_3)_2CHOH +$
$NO + HCN +$ trace of N_2O

Temperature of 181°

Measured the reaction by infrared analysis.

6. Butyl nitrite

a. STEACIE, E. W. R., and SMITH, W. McF., 1936 (123)

$C_4H_9ONO \longrightarrow C_4H_9O + NO \longrightarrow$ decomposition products (some condensation)

Temperature of 170 to 212°

Pressure of 50 to 400 mm.

The reaction was first-order and homogeneous,

$k = 8.88 \times 10^{-4} \text{ sec.}^{-1}$ at 189.9°.

b. NAGIEV, M. F., PETROVA, Z. G., and SULTANOVA, A. I., 1956 (78)

$2C_4H_9ONO \longrightarrow 2NO + C_3H_7CHO + C_4H_9OH$

Temperature of 202.5 to 239.25°

The reaction was first-order and homogeneous,

$k = 4.35 \times 10^{13} \exp. -(36,200/RT) \text{ sec.}^{-1}$

The reaction was measured by pressure change at constant volume and temperature.

7. tert-Butyl nitrite

a. LEVY, J. B., 1956 (69)

$(CH_3)_3CONO \longrightarrow (CH_3)_2CO + NO + (CH_3)_3COH + HCN + CH_2NOH$

Temperature of 181°

The reaction was first-order.

Added NO decreased the reaction rate, HCN was replaced by iso-C_3H_7ONO in the products.

The reaction was measured by infrared analyses.

B. Aliphatic dinitrites

1. General

a. KUHN, L. P., and DeANGELIS, L., 1954 (61)

$RCH(ONO)CH(ONO)R \longrightarrow 2NO + 2RCHO + RCH(OH)CH(OH)R$

Temperature of 260 to 280°

Used flow method with nitrogen as carrier gas.

Residence time of 5 seconds.

2. Propane-1, 3-dinitrite

   a. KUHN, L. P., WRIGHT, R., and DeANGELIS, L., 1956 (62)

      $ONOCH_2CH_2CH_2ONO \longrightarrow C_2H_4 + NO + NO_2 + CO_2 + HCHO$

      Temperature of 300 to 320°

      Pressures of 5 to 760 mm.

3. Butane-1, 4-dinitrite

   a. KUHN, L. P., WRIGHT, R., and DeANGELIS, L., 1956 (62)

      $ONOCH_2CH_2CH_2CH_2ONO \longrightarrow NO + C_2H_4 + HOCH_2CH_2CH_2CHO$

      Temperature of 300 to 320°

      Pressure of 5 to 760 mm.

4. Butane-1, 3-dinitrite

   a. KUHN, L. P., WRIGHT, R., and DeANGELIS, L., 1956 (62)

      $ONOCH_2CH_2CH(CH_3)ONO \longrightarrow CH_3CHO + C_2H_4 +$

      $CH_3CH{:}CH_2 + NO$

      Temperature of 300 to 320°

      Pressure of 5 to 760 mm.

5. Pentane-1, 5-dinitrite

   a. KUHN, L. P., WRIGHT, R., and DeANGELIS, L., 1956 (62)

      $ONOCH_2(CH_2)_3CH_2ONO \longrightarrow NO_2 + NO + CH_2{:}CH(CH_2)_3OH$

      Temperature of 300 to 320°

      Pressure of 5 to 760 mm.

6. Pentane-2, 4-dinitrite

   a. KUHN, L. P., WRIGHT, R., and DeANGELIS, L., 1956 (62)

$ONOCH(CH_3)CH_2CH(CH_3)ONO \rightarrow CH_3CHO + CH_3CH{:}CH_2 +$

$C_2H_4 + NO + NO_2$

Temperature of 300 to 320°

Pressure of 5 to 760 mm.

7. Hexane-1, 6-dinitrite

   a. KUHN, L. P., WRIGHT, R., and DeANGELIS, L., 1956 (62)

   $ONOCH_2(CH_2)_4CH_2ONO \rightarrow NO_2 + NO + HO(CH_2)_6OH$

   Temperature of 300 to 320°

   Pressure of 5 to 760 mm.

8. Hexane-2, 5-dinitrite

   a. KUHN, L. P., WRIGHT, R., and DeANGELIS, L., 1956 (62)

   $ONOCH(CH_3)CH_2CH_2CH(CH_3)ONO \rightarrow NO + C_2H_4 +$

   $CH_3CHO + CH_3CH(OH)CH_2CH_2COCH_3$

   Temperature of 300 to 320°

   Pressure of 5 to 760 mm.

9. 2, 5-Dimethylhexane-2, 5-dinitrite

   a. KUHN, L. P., WRIGHT, R., and DeANGELIS, L., 1956 (62)

   $ONOC(CH_3)_2CH_2CH_2C(CH_3)_2ONO \rightarrow NO + C_2H_4 + (CH_3)_2CO$

   Temperature of 300 to 320°

   Pressure of 5 to 760 mm.

XIII. NITRO COMPOUNDS

$[RNO_2]$

A. Aliphatic nitro compounds

1. Nitromethane

a. TAYLOR, H. A., and VESSELOVSKY, V. V., 1935 (136)

$CH_3NO_2 \longrightarrow CH_3NO + O$

The reaction was unimolecular and homogeneous with an activation energy of 61,000 cal./mole.

b. COTTRELL, T. L., and REID, T. J., 1950 (29)

$CH_3NO_2 \longrightarrow CH_4 + CO + NO +$ small amounts of CO_2 and H_2

Temperature of 380 to 430°

Pressure of 200 to 350 mm.

The reaction was first-order and homogeneous,

$k = 10^{14.36} \text{ exp. } -(52,700/RT) \text{ sec.}^{-1}$

k increased with pressure

c. FRÉJACQUES, C., 1950 (38)

Temperature of 310 to 440°

Pressure of 4 to 40 mm.

The reaction was first-order.

Studied the effects of N_2, H_2O, NO, O_2, H_2 and $C_2H_5^{\cdot}$ on the reaction.

d. COTTRELL, T. L., GRAHAM, T. E., and REID, T. J., 1951 (27)

$CH_3NO_2 \longrightarrow CH_3^{\cdot} + NO_2$

$CH_3^{\cdot} + NO_2 \longrightarrow NO + CH_4 + CO + H_2O +$

small amounts of CO_2, C_2H_6, C_2H_4 and N_2O

Temperature of 380 to 430°

Pressure of 200 to 400 mm.

The reaction was first-order and homogeneous, nonchain free-radical reaction, $k = 10^{14.6} \exp. -(53,600/RT) \sec.^{-1}$

The reaction was measured by the static method.

The dissociation energy of the C-N bond was 53, 000 cal. /mole.

e. HILLENBRAND, L. J., JR., and KILPATRICK, M. L., 1951 (46), 1953 (47)

$CH_3NO_2 \longrightarrow CH_3^{\cdot} + NO_2$

$CH_3^{\cdot} + NO_2 \longrightarrow HCHO +$ other decomposition products

Temperature of 420 to 480°

The reaction was first-order,

$k = 2.7 \times 10^{13} \exp. -(50,000/RT) \sec.^{-1}$

The reaction was studied by the flow method using nitrogen as a carrier gas.

f. MUELLER, K. H., 1955 (77)

$CH_3NO_2 \longrightarrow CO_2 + CO + CH_4 + HCN + NO + N_2 + H_2O +$

small amounts of CH_3CN, C_2H_5CN, CH_2O and N_2O

Temperature of 355°

Pressure of 180 to 300 psia.

Large amounts of NO_2 needed for inhibition and was effective only in the later stages of the reaction.

The major carbon compound was HCN.

Proposed mechanisms:

$$CH_3NO_2 \longrightarrow CH_3NO^{\bullet} + O^{\bullet}$$

$$CH_3NO_2 + O^{\bullet} \longrightarrow \text{products}$$

$$CH_3NO_2 \longrightarrow CH_3^{\bullet} + NO_2$$

$$CH_3^{\bullet} + CH_3NO_2 \longrightarrow CH_2NO_2 + CH_4$$

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow C_2H_6$$

$$CH_3NO^{\bullet} \longrightarrow CH_2NOH$$

$$CH_2NOH \longrightarrow HCN + H_2O$$

g. GRAY, P., YOFFE, A. D., and ROELAAR, L., 1955 (43)

$$CH_3NO_2 \longrightarrow HCHO + CO + CH_4 + N_2$$

Temperature of 240 to 800°

Free-radicals sensitized the decomposition at temperature 200° lower than were normally needed.

Flow system was used.

2. Nitroethane

a. FRÉJACQUES, C., 1950 (38)

Temperature of 310 to 440°

Pressure of 4 to 40 mm.

The reaction was first-order.

Studied the effect of N_2, H_2O, NO, O_2, H_2 and $C_2H_5^{\bullet}$ on the reaction.

b. COTTRELL, T. L., GRAHAM, T. E., and REID, T. J., 1951, (28)

$C_2H_5NO_2 \longrightarrow C_2H_4$ + NO + some oxides of carbon

Temperature of 355 to 405°

Pressure of 50 to 300 mm.

The reaction was first-order and homogeneous (about 10% heterogeneous), $k = 10^{13.0}$ exp. $-(47,000/RT)$ sec.$^{-1}$ (for the homogeneous reaction.)

c. WILDE, K. A., 1956 (144)

$C_2H_5NO_2 \longrightarrow C_2H_4$ + NO + H_2O + small amounts of HCN, NO_2, CO_2 and aldehyde

Temperature of 414 to 459°

Atmospheric pressure

The reaction was first-order.

At 414 to 442°, $k = 10^{11.35 \pm 0.9}$ exp. $-(41,400 \pm 1,100)/RT$ sec.$^{-1}$

d. GRAY, P., YOFFE, A. D., and ROELAAR, L., 1955 (43)

$C_2H_5NO_2 \longrightarrow$ HCHO + CO + CH_4 + N_2 + other products

Temperature of 240 to 800°

Free-radicals sensitized the decomposition at temperatures 200° lower than were normally needed.

Flow system was used.

3. Nitropropane

a. FRÉJACQUES, C., 1950 (38)

Temperature of 310 to 440°

Pressure of 4 to 40 mm.

The reaction was first-order.

Studied the effects of N_2, H_2O, NO, O_2, H_2 and $C_2H_5^{\bullet}$ on the reaction.

b. WILDE, K. A., 1956 (144)

$C_3H_7NO_2 \longrightarrow C_3H_6 + NO + H_2O +$ small amounts of HCN, NO_2, CO_2 and aldehyde

Temperature of 414 to 459°

The reaction was first-order at 414 to 442°,

$k = 10^{13.4}$ exp. $-(47,700/RT)$ sec.$^{-1}$

c. GRAY, P., YOFFE, A. D., and ROELAAR, L., 1955 (43)

$C_3H_7NO_2 \longrightarrow HCHO + CO + CH_4 + N_2 +$ other products

Temperature of 240 to 800°

Free-radicals sensitized the decomposition at temperatures 200° lower than were normally needed.

Flow system was used.

4. Nitroisopropane

a. FREJACQUES, C., 1950 (38)

Temperature of 310 to 440°

Pressure of 4 to 40 mm.

The reaction was first-order.

Studied the effects of N_2, H_2O, NO, O_2, H_2 and $C_2H_5^{\bullet}$ on the reaction.

b. WILDE, K. A., 1956 (144)

$(CH_3)_2CHNO_2 \longrightarrow NO + H_2O +$ olefin + small amounts of HCN, NO_2, CO_2 and aldehyde.

$k = 10^{13.0}$ exp. $-(39,000/RT)$ sec.$^{-1}$

Proposed acid-form of activated complex.

The reaction was studied by the flow method using nitrogen as a carrier gas.

c. GRAY, P., YOFFE, A. D., and ROELAAR, L., 1955 (43)

$(CH_3)_2CHNO_2 \longrightarrow HCHO + CO + CH_4 + N_2 +$ other products

Temperature of 240 to 800°

Free-radicals sensitized the decomposition at temperatures 200° lower than were normally needed.

Flow system was used.

B. Aliphatic dinitro compounds

1. N,N-Dinitroethylene diamine

a. ROBERTSON, A. J. B., 1948 (101)

Temperature of 184 to 254°

The reaction was first-order, $t_{1/2}$ at 184° = 43 seconds, at 254° $t_{1/2} = 1/2$ second.

C. Aromatic trinitro compounds

1. 2, 4, 6-Trinitrophenylmethylnitramine

a. ROBERTSON, A. J. B., 1948 (101)

Temperature of 184 to 254°

XIV. MISCELLANEOUS NITROGEN COMPOUNDS

A. Oximes $[R_2C{:}NOH]$

1. Formaldehyde oxime

a. TAYLOR, H. A., and BENDER, H., 1941 (131)

$$CH_2NOH \longrightarrow HCN + H_2O$$

$$HCN + H_2O \longrightarrow CO + NH_3 + N_2 + C_2H_6 + H_2$$

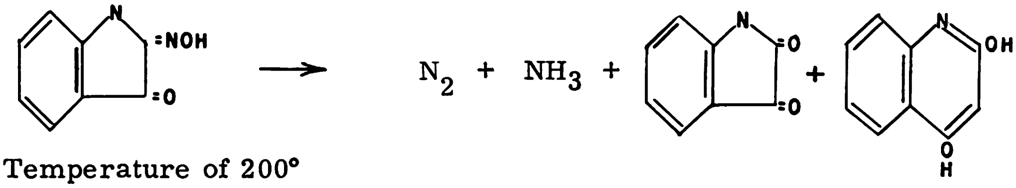
The reaction was first-order and thought to be heterogeneous,

$$k = 10^{9.5} \text{ exp. } -(39,000/RT) \text{ sec.}^{-1}$$

The reaction was accelerated by nitric oxide and traces of air.

2. Isatin 2-oxime

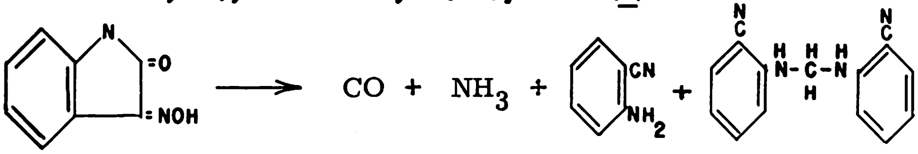
a. BARGELLINI, G., and TURI, C. J., 1954 (7)



Temperature of 200°

3. Isatin 3-oxime

a. BARGELLINI, G., and TURI, C. J., 1954 (7)



Temperature of 220°

B. Phenylurethans (Carbanilates)

1. Cyclohexyl carbanilate

a. ILLARI, G., MARENGHI, I., and TARANTELLI, T., 1953 (51)

$$C_6H_5NHCOOC_6H_{11} \longrightarrow \text{tarry residue}$$

Temperature above 200°

2. Benzyl carbanilate

   a. ILLARI, G., MARENGHI, I., and TARANTELLI, T., 1953 (51)

   $C_6H_5NHCOOCH_2C_6H_5 \longrightarrow$ tarry residue

   Temperature above 200°

3. Naphthyl carbanilate

   a. ILLARI, G., MARENGHI, I., and TARANTELLI, T., 1953 (51)

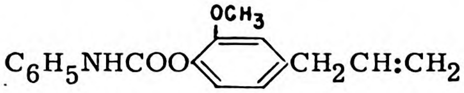
   $C_6H_5NHCOOC_{10}H_7 \longrightarrow C_6H_5NCO$ + phenolic compounds +

   $CO(NHC_6H_5)_2$ (sometimes)

   Temperature of 235°

4. Eugenyl carbanilate

   a. ILLARI, G., MARENGHI, I., and TARÀNTELLI, T., 1953 (51)



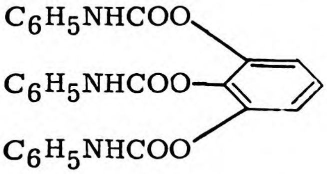
   $\longrightarrow C_6H_5NCO$ + phenolic

   compounds + $CO(NHC_6H_5)_2$ (sometimes)

   Temperature of 235°

5. Pyrogallyl carbanilate

   a ILLARI, G., MARENGHI, I., and TARANTELLI, T., 1953 (51)



   $\longrightarrow C_6H_5NCO$ + phenolic compounds +

   $CO(NHC_6H_5)_2$ (sometimes)

   Temperature of 235°

PART II

SULFUR COMPOUNDS

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PART II

SULFUR COMPOUNDS

I. DISULFIDES

[RSSR]

A. Aliphatic disulfides

1. 2, 3-Dithiabutane

   a. COOPE, J. A. R., and BRYCE, W. A., 1954 (26)

   $CH_3SSCH_3 \longrightarrow CH_3SH + (1/n)(CH_2S)_n$

   Hydrogen sulfide production competed with the above reaction.

   Temperature of 316 to 373°

   Pressure of 24 to 230 mm.

   The reaction was first-order,

   $k = 2 \times 10^{13} \text{ exp. } -(45,000/RT) \text{ sec.}^{-1}$

   The reaction was catalyzed by the products and hydrogen sulfide had the least activity.

   There was a reproducible induction period.

   b. BRAYE, E. H., SEHON, A. H., and DARWENT, B. deB., 1955 (17)

   Decomposition proceeded by a molecular rearrangement.

2. 3, 4-Dithiahexane

   a. COOPE, J. A. R., and BRYCE, W. A., 1954 (26)

   $C_2H_5SSC_2H_5 \longrightarrow \text{decomposition products}$

Temperature of 318°

The reaction was first-order,

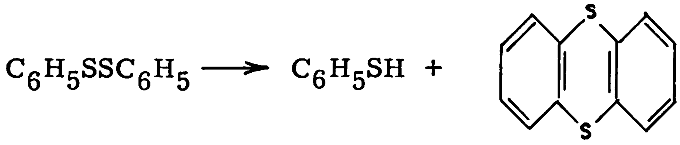
$$k = 2 \times 10^{13} \text{ exp. } -(45,000/RT) \text{ sec.}^{-1}$$

The pressure-temperature curves showed two stages.

B. Aromatic disulfides

1. Diphenylthiaethane

a. SCHÖNBERG, A., MUSTAFA, A., and ASKAR, W., 1949 (106)



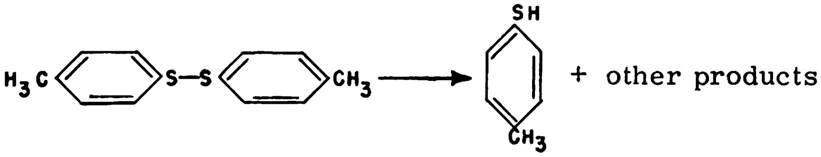
$C_6H_5SSC_6H_5 \longrightarrow C_6H_5SH +$

Temperature of 288°

Heated for six hours in the absence of air.

2. 1, 2-Di(4-methylphenyl)dithiaethane

a. SCHÖNBERG, A., and MUSTAFA, A., 1949 (105)



Temperature of 270°

Heated for six hours.

3. 1, 1, 4, 4-Tetraphenyl-2, 3-dithiabutane

a. MOREAU, R. C., 1955 (76)

$$(C_6H_5)_2CHSSCH(C_6H_5)_2 \longrightarrow (C_6H_5)_2CH_2 + (C_6H_5)_2CS + S +$$
$$(C_6H_5)_2CHCH(C_6H_5)_2 + (C_6H_5)_2C{:}C(C_6H_5)_2 + H_2S$$

Temperature of 155 to 300°

Heated for five minutes.

II. SULFIDES

[RSR, RSRSR, RSRSRSR]

A. Aliphatic sulfides

1. 2-Thiapropane

a. BRAYE, E. H., SEHON, A. H., and DARWENT, B. deB., 1955 (17)

Preliminary studies showed that the reaction was a free-radical reaction.

2. 3-Thiapentane

a. TRENNER, N. R., and TAYLOR, H. A., 1933 (142)

$C_2H_5SC_2H_5 \longrightarrow$ decomposition products

Temperature of 380 to 410°

Pressure of 50 to 400 mm.

The reaction was unimolecular and homogeneous with an activation energy of about 40,000 cal./mole.

The work was done in glass poisoned by the reaction products.

Proposed $C_2H_5SH{:}SHC_2H_5$ as an intermediate.

b. RUDENKO, M. G., and GROMOVA, V. N., 1951 (102)

At a temperature of 400° H_2S evolution began.

Steel shavings used as a catalyst.

B. Aromatic sulfides

1. (2-Thiapropyl)benzene

a. BRAYE, E. H., SEHON, A. H., and DARWENT, B. deB., 1955 (17)

$C_6H_5CH_2SCH_3$ ⟶ decomposition products

The reaction was a first-order, homogeneous, free-radical reaction with an activation energy of 51,000 ± 2,000 cal./mole.

The reaction was studied by the flow method using toluene as a carrier gas.

2. Cyclohexylphenylthiamethane

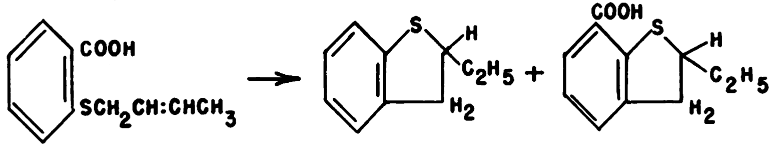
   a. RUDENKO, M. G., and GROMOVA, V. N., 1951 (102)

   At a temperature of 350° H_2S evolution began.

   Steel shavings used as a catalyst.

3. 1-Thia-3-phenylbenzoic acid

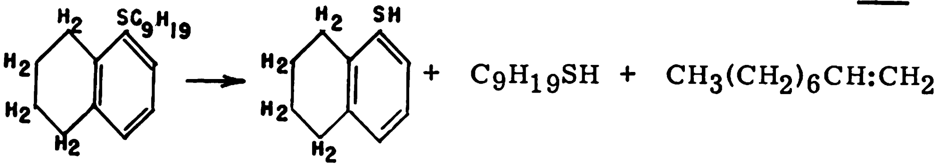
   a. PETROPOULOS, J. C., McCALL, M. A., and TARBELL, D. S., 1953 (85)



   Temperature of 260°

4. 8-(1-Thiadecyl)tetralin

   a. TITS-SKVORTSOVA, I. N., and DANILOVA, T. A., 1956 (140)

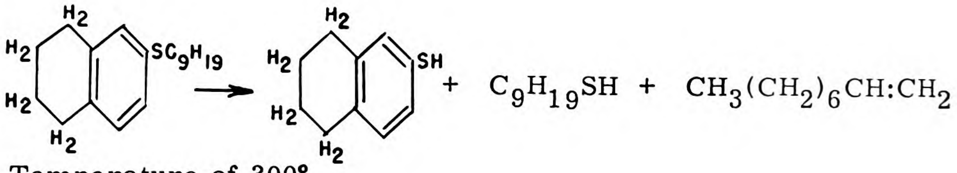


   Temperature of 300°

   Used aluminosilicate as catalyst.

5. 7-(1-Thiadecyl)tetralin

   a. TITS-SKVORTSOVA, I. N., and DANILOVA, T. A., 1956 (140)

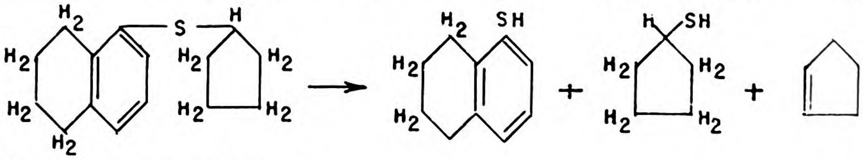


Temperature of 300°

Used aluminosilicate as catalyst.

6. Cyclopentyltetralylthiamethane

   a. TITS-SKVORTSOVA, I. N., and DANILOVA, T. A., 1956 (140)



Temperature of 300°

Used aluminosilicate as catalyst.

C. Double sulfides

1. 1, 4-Diphenyl-1, 4-dithiabutane

   a. LANDAU, E. F., and IRANY, E., 1949P (64)

$C_6H_5SCH_2CH_2SC_6H_5 \rightarrow C_6H_5SH + C_6H_5SCH:CH_2$

Temperature of 350 to 500°

Glass bead packing used.

The reaction was performed in the absence of air.

2. 1, 2, 3, 4-Tetraphenyl-1, 4-dithia-2-butene

   a. SCHÖNBERG, A., and MUSTAFA, A., 1949 (105)

$C_6H_5(C_6H_5S)C:C(SC_6H_5)C_6H_5 \rightarrow C_6H_5SH + C_6H_5C\vdots CC_6H_5$

Temperature of 270°

Heated for six hours.

D. Triple sulfides

1. 2, 5, 8-Trithianonane

a. CHARNOCK, R. J., and MOGGRIDGE, R. C. G., 1946 (23)

$$CH_3SCH_2CH_2SCH_2CH_2SCH_3 \longrightarrow CH_3SH + CH_3SCH{:}CH_2 + CH_3S(CH_2)_2SH + (CH_3SCH_2CH_2SCH_2)_2 + CH_3SCH_2CH_2SCH_3$$

Heated for 2.5 hours.

III. THIOLS

[RSH]

A. Aliphatic thiols

1. Methanethiol

a. SEHON, A. H., and DARWENT, B. deB., 1954 (109)

$CH_3SH \longrightarrow$ decomposition products

The reaction was free-radical with an activation energy of 67,000 cal./mole.

The reaction was studied by the flow method using toluene as a carrier gas.

2. Ethanethiol

a. TRENNER, N. R., and TAYLOR, H. A., 1933 (142)

$C_2H_5SH \longrightarrow$ decomposition products

Temperature of 380 to 410°

Pressure of 50 to 400 mm.

The reaction was homogeneous with an activation energy of 44,000 cal./mole.

There was an induction period.

Used a glass vessel.

Postulated $C_2H_5SH{:}SHC_2H_5$ as an intermediate product.

b. MALISOFF, W. M., and MARKS, E. M., 1933 (73)

Polemical with TRENNER (2, a)

c. TRENNER, N. R., and TAYLOR, H. A., 1933 (143)

The addition of 10 gases did not materially alter the latter course of the reaction.

d. SEHON, A. H., and DARWENT, B. deB., 1954 (109)

$C_2H_5SH \longrightarrow C_2H_4 + H_2S$

The reaction was heterogeneous with an activation energy of 48,000 to 55,000 cal./mole. The activation energy decreased with decreasing temperature.

e. BOIVIN, J. L., and MacDONALD, R., 1955 (11)

$C_2H_5SH \longrightarrow C_2H_4 + H_2S +$ small amounts of H_2, S, C_2H_6, CH_4, CS_2, $(C_2H_5)_2S$, COS and thiophene

Temperature of 400 to 700°

Used sulfides of Cd, Ni, Co, Cu and Fe as catalysts.

With catalysts, maximum yield of unsaturated products was at 500 to 600°; without catalysts, a temperature of 600 to 700° is optimum.

Used a flow system.

3. 1-Butanethiol

a. RUDENKO, M. G., and GROMOVA, V. N., 1951 (102)

At a temperature of 200° H_2S evolution began.

Used steel shavings as catalyst.

4. 2-Methyl-1-propanethiol

a. RUDENKO, M. G., and GROMOVA, V. N., 1951 (102)

At a temperature of 225 to 250° H_2S evolution began.

Used steel shavings as a catalyst.

5. 2-Methyl-2-propanethiol

   a. THOMPSON, C. J., MEYER, R. A., and BALL, J. S., 1952 (138)

      $(CH_3)_3CSH \longrightarrow H_2S + S + (CH_3)_2C{:}CH_2 + (CH_3)_3CH$

      Temperature of 300 to 500°

      Atmospheric pressure

      The reaction proceeded by a free-radical chain mechanism.

      Flow method was used.

6. 1-Pentanethiol

   a. THOMPSON, C. J., MEYER, R. A., and BALL, J. S., 1952 (139)

      $C_5H_{11}SH \longrightarrow C_3H_7CH{:}CH_2 + H_2S + (C_5H_{11})_2S$ (?)

      Temperature of 350 to 500°

      Atmospheric pressure

      The reaction proceeded by a free-radical chain mechanism.

      Flow method was used.

7. 1-Hexanethiol

   a. RUDENKO, M. G., and GROMOVA, V. N., 1951 (102)

      At a temperature of 200° H_2S evolution began.

      Used steel shavings as a catalyst.

B. Aromatic thiols

1. Phenylmethanethiol

   a. SEHON, A. H., and DARWENT, B. deB., 1954 (109)

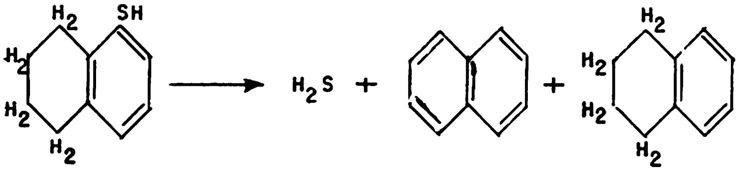
      $C_6H_5CH_2SH \longrightarrow$ decomposition products

The reaction was a first-order, homogeneous free-radical reaction with an activation energy of 53, 000 ± 20, 000 cal. /mole.

The reaction was studied by the flow method using toluene as a carrier gas.

2. 1 – Tetralinthiol

a. TITS-SKVORTSOVA, I. N., and DANILOVA, T. A., 1956 (140)

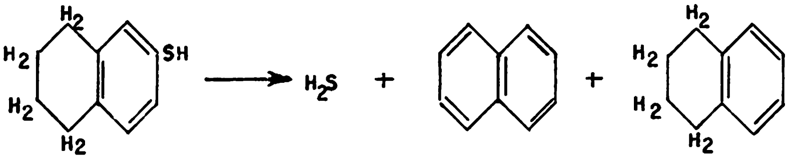


Temperature of 300°

Used aluminosilicate as catalyst.

3. 2 – Tetralinthiol

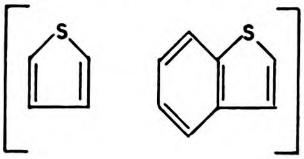
a. TITS-SKVORTSOVA, I. N., and DANILOVA, T. A., 1956 (140)



Temperature of 300°

Used aluminosilicate as catalyst.

IV. THIOPHENES



A. Aliphatic thiophenes

1. Thiophene

a. RUDENKO, M. G., and GROMOVA, V. N., 1951 (102)

At a temperature 500° there was no H_2S evolution.

Used steel shavings as catalyst.

2. 2, 5-Dimethylthiophene

a. RUDENKO, M. G., and GROMOVA, V. N., 1951 (102)

At a temperature of 475° very slight H_2S evolution.

Used steel shavings as catalyst.

B. Condensed thiophenes

1. Benzo [b] thiophene 1, 1-dioxide

a. BORDWELL, F. G., McKELLIN, W. H., and BABCOCK, D., 1951 (12)

Benzo [b] thiophene 1, 1-dioxide → SO_2 + 6a, 11b-dihydronaphtho [2, 1-b] benzo [b] thiophene 7, 7-dioxide

V. XANTHATES

[ROC(S)SM]

A. Aliphatic xanthates

1. Cholesterylxanthate

a. O'CONNER, G. L., and NACE, H. A., 1953 (80)

Cholesterylxanthate ⟶ decomposition products

The reaction was first-order with an activation energy of 44,100 cal./mole.

The reaction had a negative entropy of activation.

PART III

COMPOUNDS CONTAINING NITROGEN AND SULFUR

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PART III

COMPOUNDS CONTAINING NITROGEN AND SULFUR

I. THIOACID AMIDES

[RC(S)NHR]

A. Aromatic thioacid amides

1. General

   a. BOUDET, R., 1951 (14)

   $RC(S)NHCH_2C_6H_5 \longrightarrow RCN + (C_6H_5CH{:})_2 + H_2S$

   $RC(S)NHCH_2C_6H_5 \longrightarrow C_6H_5CH_3 + RCN + (C_6H_5CH{:})_2 + H_2S + NH_3$

   The first reaction was found at temperatures above 250° and the second reaction at temperatures below 250°.

2. N-Benzylthiobenzamide

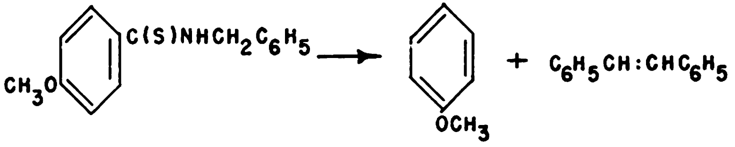
   a. BOUDET, R., 1949 (13)

   $2C_6H_5C(S)NHCH_2C_6H_5 \longleftrightarrow 2C_6H_5C(SH){:}NCH_2C_6H_5 \longrightarrow 2H_2S + 2C_6H_5CN + 2C_6H_5C{:}NCHC_6H_5 + C_6H_5CH{:}CHC_6H_5$

   Temperature of 400°

3. N-Benzylthioanisamide

   a. BOUDET, R., 1949 (13)

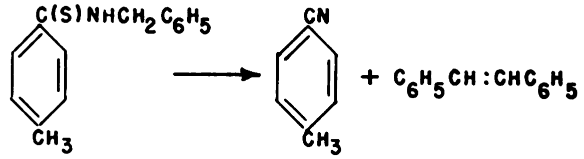


   Temperature of 400°

Original from THE OHIO STATE UNIVERSITY

4. N-Benzylthio-p-toluamide

   a. BOUDET, R., 1949 (13)

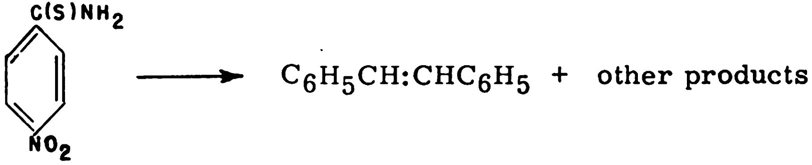


$C(S)NHCH_2C_6H_5$ → CN + $C_6H_5CH{:}CHC_6H_5$

Temperature of 400°

5. p-Nitrothiobenzamide

   a. BOUDET, R., 1949 (13)

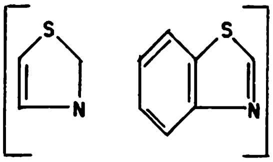


$C(S)NH_2$ → $C_6H_5CH{:}CHC_6H_5$ + other products

Temperature of 400°

The reaction was violent.

II. THIAZOLES



A. Condensed thiazoles

1. 2-(2-Cyclohexen-1-ylthio)benzothiazole

   a. MOORE, C. G., and WAIGHT, E. S., 1952 (75)

2-(2-Cyclohexen-1-ylthio)benzothiazole → benzene + cyclohexene + thiazole + 3-(2-cyclohexen-1-ylthio)benzothiazole

Temperature of 200°

Heated for 48 hours.

At a temperature of 100° the isomerization reaction was exclusive.

III. THIOCYANATES

A. Aromatic thiocyanates

1. Aniline thiocyanate

a. GUPTA, R. D., and GUPTA, N. P., 1950 (44)

$C_6H_5NH_2 . HSCN \longrightarrow HSCN + C_6H_5NH_2 + NH_4SCN$

Temperature of 135°

Heated for 2.5 hours.

Proposed mechanisms:

$C_6H_5NH_2 . HSCN \rightleftharpoons C_6H_5NHCSNH_2$

$C_6H_5NHCSNH_2 \longrightarrow C_6H_5N{:}C{:}S + NH_3$

$C_6H_5NH_2 . HSCN + NH_3 \rightleftharpoons C_6H_5NH_2 + NH_4SCN$

$C_6H_5NH_2 + C_6H_5N{:}C{:}S \rightleftharpoons (C_6H_5NH)_2CS$

IV. THIURAM DISULFIDES

[$R_2NC(S)SSC(S)NR_2$]

A. Aliphatic thiuram disulfides

1. bis(Dimethyldithiocarbamoyl)disulfide

   a. SAHARABUDHEY, R. H., and RADHAKRISHNAN, K. L., 1954 (104)

   $(CH_3)_2NC(S)SSC(S)N(CH_3)_2 \longrightarrow CS_2 + S + (CH_3)_2NC(S)N(CH_3)_2$

   and small amounts of $(CH_3)_2NC(S)SH.HN(CH_3)_2$ and $(CH_3)_2NC(S)SC(S)N(CH_3)_2$

   Temperature of 150 to 200°

2. bis(Diethylthiocarbamoyl)disulfide

   a. SAHARABUDHEY, R. H., and RADHAKRISHNAN, K. L., 1954 (104)

   $(C_2H_5)_2NC(S)SSC(S)N(C_2H_5)_2 \longrightarrow CS_2 + S + (C_2H_5)_2NC(S)N(C_2H_5)_2$

   and small amounts of $(C_2H_5)_2NC(S)SH.HN(C_2H_5)_2$ and $(C_2H_5)_2NC(S)SC(S)N(C_2H_5)_2$

   Temperature of 200°

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